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II Semester 1934-35

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The Stereochemistry of Triarylmethyl Radicals

G. Karagunis and G. Drikes, Z.physik. Chem., 26B, 428-38 (1934)

(Authors located at the University of Athens and have had no previous publications.)

Until now experiments intended to determine the steric configuration of free triarylmethyl radicals have been unsuccessful.

The irradiation of asymmetric radicals with circularly polarized light during treatment with halogens gave a mixture of halides which was optically active. A mechanism was postulated as follows: The radicals are of tetrahedral form and exist as a mixture of the two possible antipodes. Irradiation results in the activation of one of the forms, causes chlorination of it, and consequent optical activity.

By using $\text{Me}(4, \text{MeC}_6\text{H}_4)(p\text{-EtC}_6\text{H}_4)\text{C}\cdot$ with circularly polarized light of wavelength 4300\AA and introducing Cl_2 at 0°C , a maximum rotation of 0.2° was obtained. For the compound, $\text{Ph}(\text{PhC}_6\text{H}_4)(\alpha\text{C}_{10}\text{H}_7)\text{C}\cdot$, rotations up to 0.1° with light of 5390\AA were given. The phenomenon was anisotropic, i.e. with light polarized to the right, rotation occurred in one direction and with light of the same frequency but polarized in the opposite to the left, the rotation was in the opposite direction.

Seminar Report

M.F.Roy

March 24, 1935.

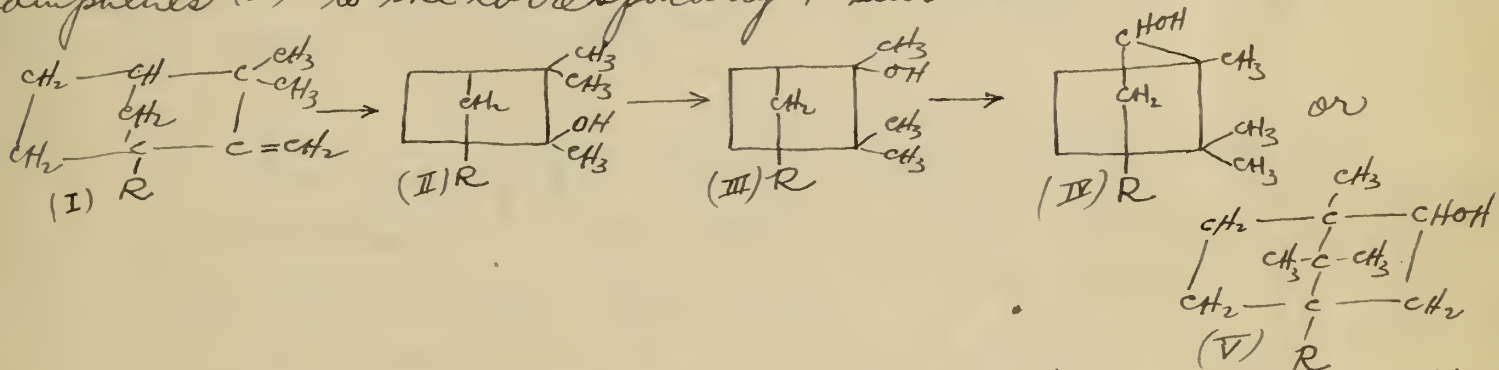
Organic Seminar, May 15, 1935.

Reported by Poe Liang

"A New Series of Homologs of the Camphor Group"

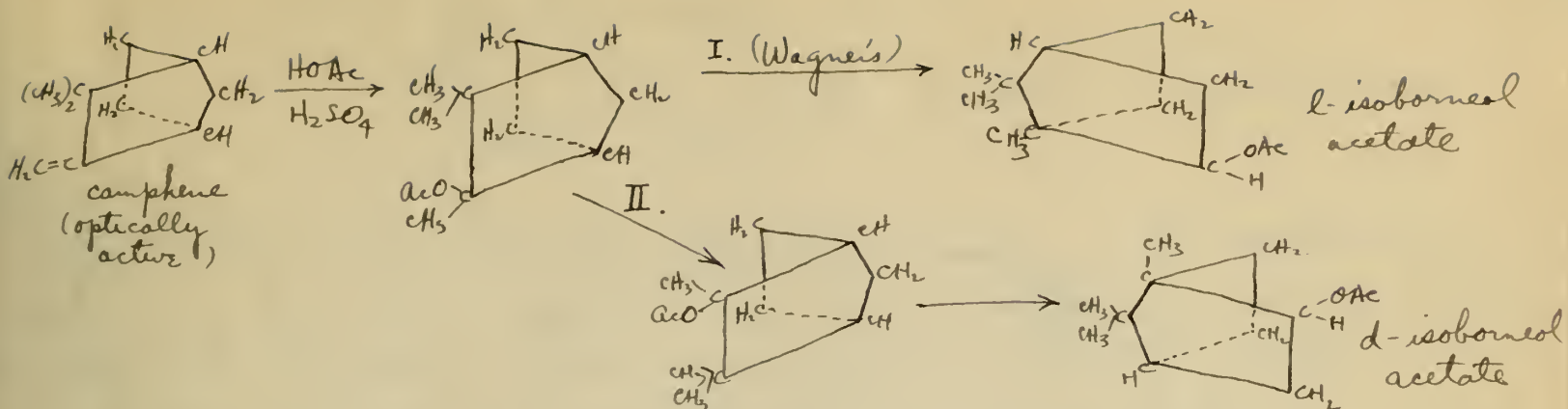
G. S. S. Nametkin and coworkers, Ann., 516, 199 (1935); J. pr., [2] 124, 144 (1930); Ann., 459, 144 (1927).

Nametkin and coworkers have shown that transformation of hydrocarbons of camphor type into alcohols of isoborneol type as well as the reverse process do not proceed in only one direction (camphene rearrangement of type I, or Wagner's rearrangement), but may also be accompanied by an isomerization of another manner (camphene rearrangement of type II). This latter type of rearrangement may be illustrated by the following scheme for the transformation of α -substituted camphenes (I) to the corresponding 4-substituted isoborneol (IV-V):



To serve as proof for this proposition may be mentioned some recent work by other investigators in which the above scheme proposed by Nametkin for the rearrangement of camphene was applied with success for the explanation of an extremely interesting attendant phenomenon of this reaction, namely that of the partial or complete racemization.

This phenomenon which takes place during the transformation of camphene into isoborneol can be easily explained if we assume that the rearrangement which results with isobornyl acetate may proceed following course I as well as course II according to the proposed scheme:



The isoborneols thus formed according to the different courses of the rearrangement are mirror images of each other and may therefore under proper conditions in which they are formed simultaneously and in equal quantities give a racemic mixture. But if the process is carried out under rigorous conditions, the reaction will proceed in only one specific direction with the result of the formation of an optically active end-product.

The course of formation of 4-propyl-isoborneol from d-propyl bornyl alcohol is discussed in detail with reference to the corresponding methyl compounds. The structure of the various intermediates and end-products are supported by sound experimental evidences.

Reaction of the Ziegner Reagent on Hydroxymethylene ketones.

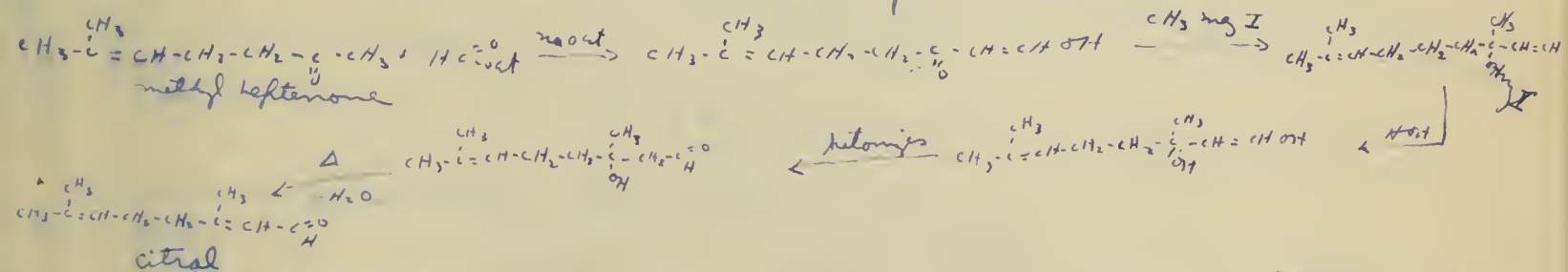
Robt. E. Meyer. Helv. 18101, 279, 282, 305, (1935)

author works at Basel, anstalt für anorganische chemie
Field: Taphanes.

Loren (Bull. Soc. [3] 21 969 (1899)) attempted to prepare 1,3 keto aldehydes by the reaction of ethylformate on certain methyl ketones but obtained a compound having no aldehydic properties which was shown to be in the stable enol form i.e.

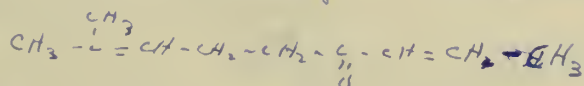


Meyer calls this compound a hydroxymethylene ketone and postulated that it owed its stability to the proximity of the keto-group. He suggested that if the influence of the keto group were removed the compound would change to the aldehyde form. This then might lead to a synthesis of α - β unsaturated aldehydes. i.e.

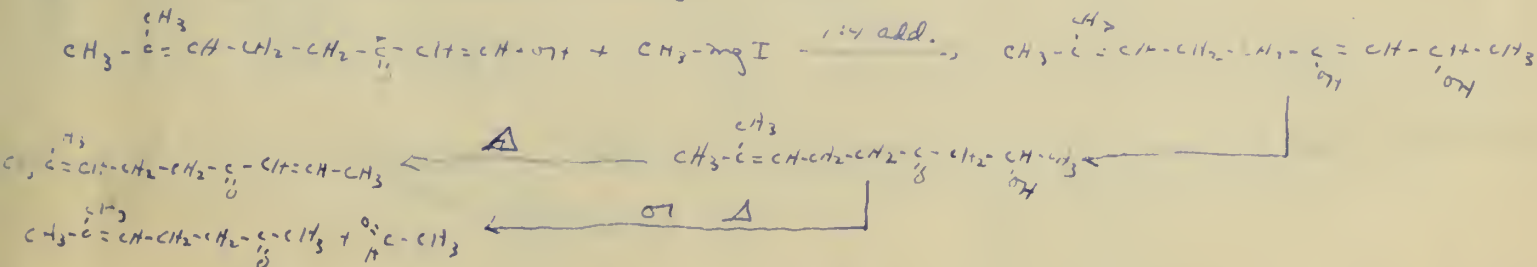


Meyer carried out this series of reactions and by the condensation of the methyl ketone with CH_3MgI obtained a compound which showed a series of aldehyde reactions and which could not be obtained pure. Heating a large sample of this compound gave a new compound $\text{C}_{10}\text{H}_{16}\text{O}$ isomeric but not identical with citral and also considerable quantities of methyl heptenone and acetaldehyde.

By a series of reactions Meyer proved that the compound $\text{C}_{10}\text{H}_{16}\text{O}$ was



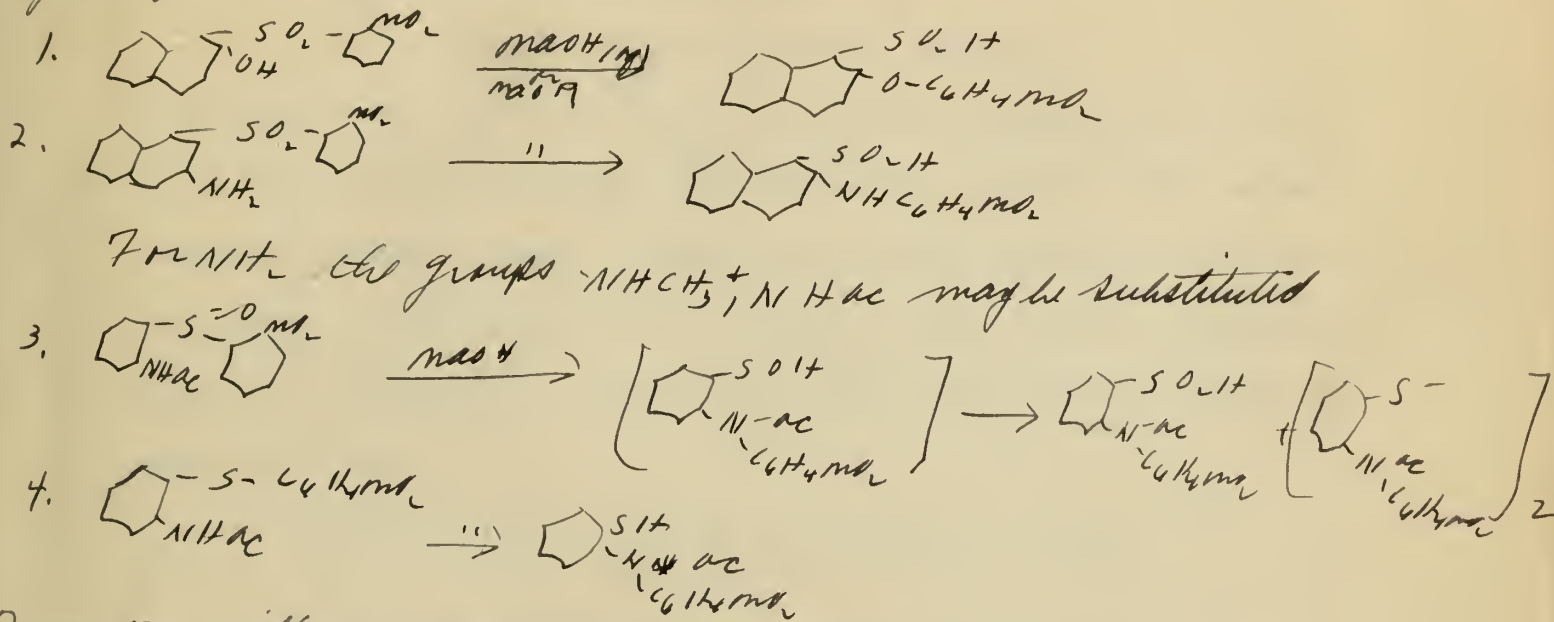
which would be formed by 1:4 addition of the Ziegner reagent to the hydroxymethylene ketone. i.e.



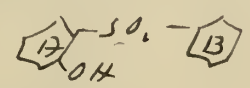
So far as the author could find 1:4 addition took place exclusively so he concludes that α - β unsaturated aldehydes of the citral type cannot be made by this method. The hydroxymethylene ketones from dihydro pseudo ionone and β -ionone were likewise shown to give 1:4 additions of the Ziegner reagent.

Smiles, I. Rearrangement of α Substituted Sulfoxes, Sulfonates, + Sulphides. J.C.S. 1931, 171. (an abstract of seminar report given Apr. 3, 1935.)

A. Types of Rearrangements observed:

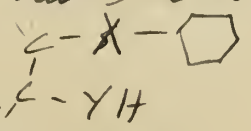


B. Factors influencing rearrangement.

1. For α OH sulfoxes, - 
 - a. α or β negative substitution in B facilitates rearrangement.
 - b. m " " " " inhibits " "
 - c. P. (or OH) " " " " facilitates " "
 - d. " " positive " " " " inhibits " "
 - e. m " negative " " " " " " "
 - f. nature of medium.

$\text{NaOC}_2\text{H}_5 > \text{NaOEt} > \text{NaOMe} > \text{NaOH}$. - arranged in decreasing order of ease of promoting rearrangement.

C. Summary of experimental results:

on the cpd. of type 

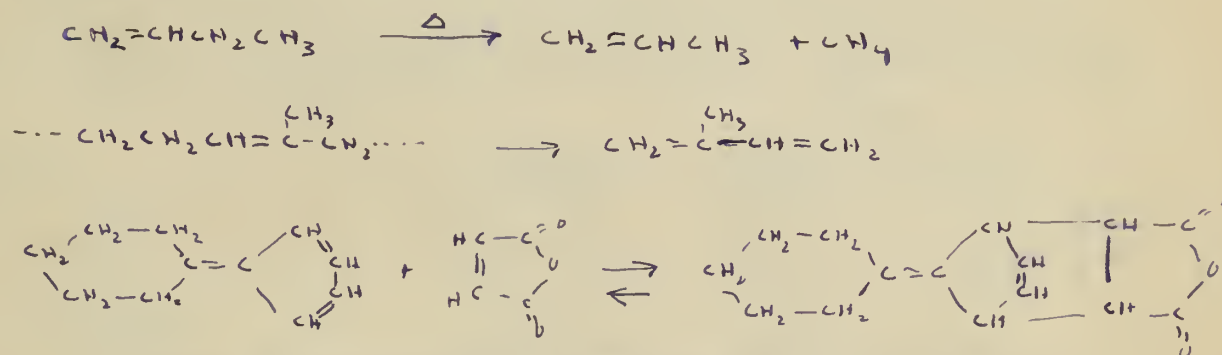
If $\text{YH} = \text{NHAc}$	then X may be SO_2 , SO , or S + Rearr. will take place.
" " = OH (aliphatic)	" " SO_2 or SO .
" " = NH_2 (arom.)	" " SO_2 or SO .
" " = OH (")	" " SO_2 or SO .
" " = SH	" " O .

THEORIES CONCERNED WITH THE SPLITTING OF THE CARBON CHAIN

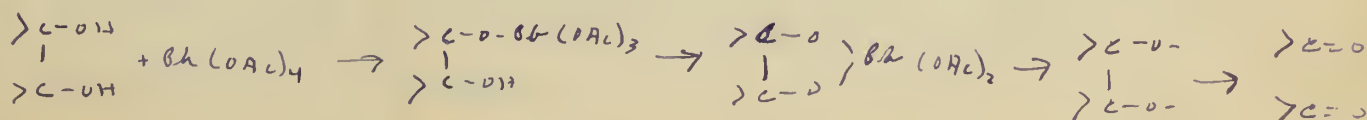
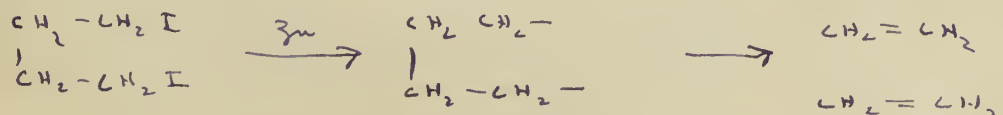
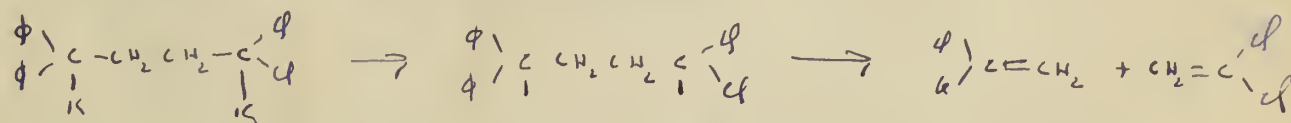
Seminar report, May 22, 1935.

By M. A. Spielman

Otto Schmidt of the Ludwigshafen Laboratory of the I-G Dye Trust has revived the old theory of alternating polarity and applied to it the mechanics of Heitler and London. As a result of his calculations he arrived at the following rule: In the splitting of a compound containing a double bond, or one in which a double bond is formed as a prelude to splitting, the break takes place between atoms 3 and 4. Examples are given.



Criegee has formulated a different theory: If two mobile groups or atoms are removed from the 1,4-positions of a molecule, a split will take place between atoms 2 and 3. Otherwise stated, the 1,4-diradical is incapable of existence, but stabilizes itself by division between atoms 2 and 3. The following are illustrations.

Schmidt, Ber., 68, 60 (1935).Criegee, ibid., 68, 665, (1935).

William Sparks

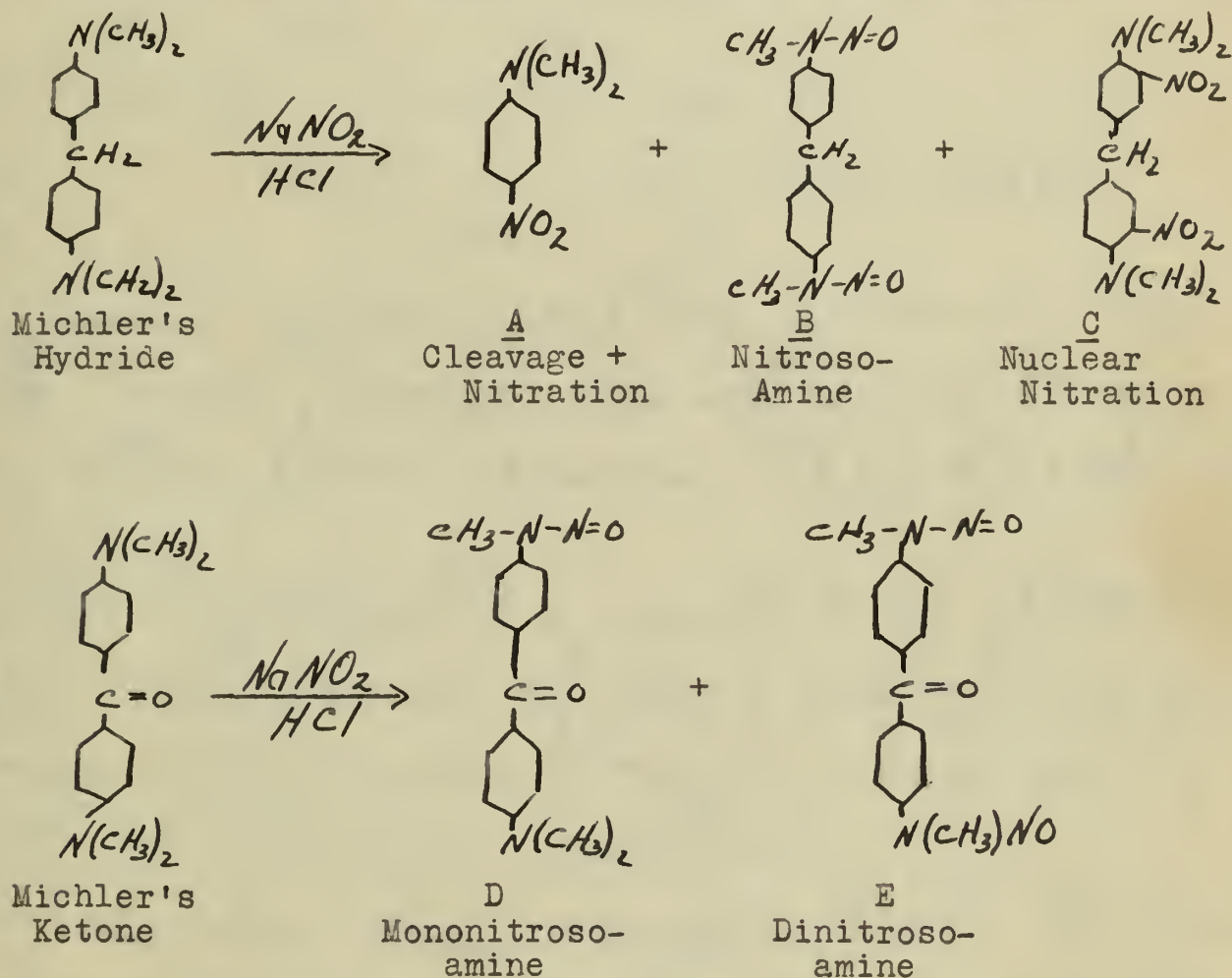
5/8/'35

7

Subject: Action of Nitrous Acid on Aromatic Tertiary Amines.

Reference: Donald and Reade, J. Chem. Soc., (1935) 53.

Summary: Michler's ketone and Michler's hydride do not follow the general rule that nitrous acid does not react with para-substituted aromatic tertiary amines. Instead they give the following products:

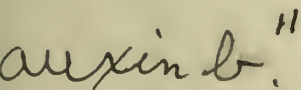
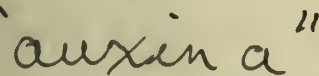


These reactions may be so controlled by regulating the acidity of the solution as to yield a maximum amount of any one of the products and a minimum of the others. A is favored by low acidity, B by medium, and C by high (9 N HCl); D by low, and E by high. The nitroso-amines are probably intermediates in the formation of the nitro compounds, since (sodium nitrate $\xrightarrow{+\text{HCl}}$ alone will not produce them.

Fritz Kögl (Utrecht)

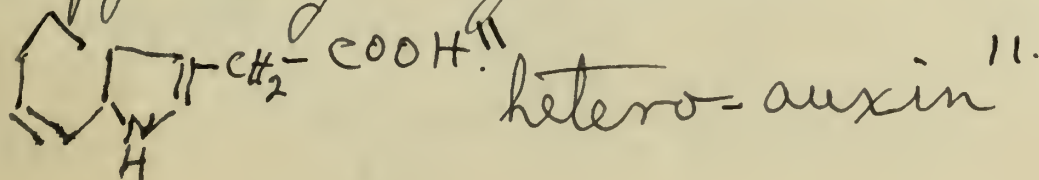
Per. 68A. 16-28

1935.



The entire investigation used only about 800 - 900 milligrams of pure substance. The human hormones and vitamins were found to be inactive.

Kögl has also discovered what he considers a pseudo hormone, active for growth but appearing only in human urine.



hetero-auxin

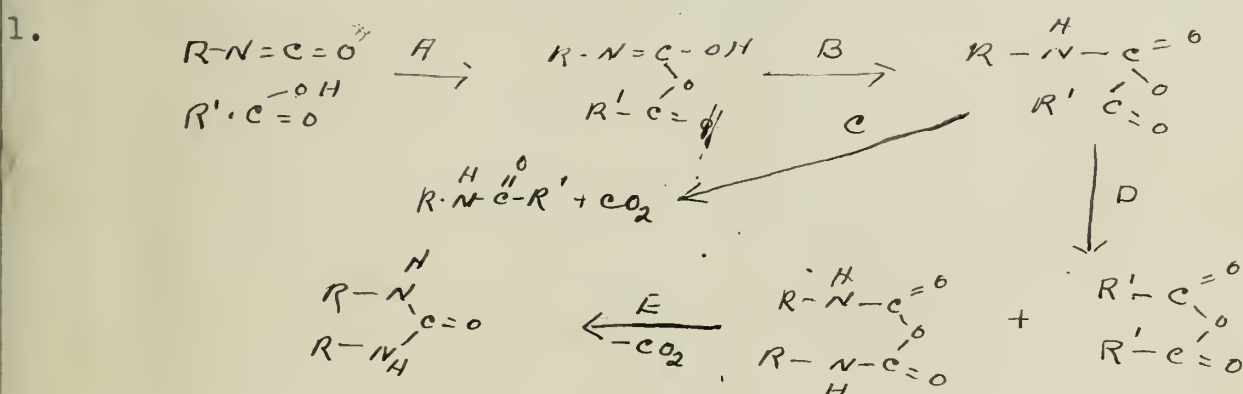
THE REACTION OF ISOCYANIC ACID ESTERS WITH ORGANIC ACIDS

I. The theory and application of the reaction for the preparation of acid anhydrides, *von C Naegli and H. Fyabgi Helv. Chim. Acta. 17 931 (1934)*
 which, *Chemisches Institut der Universität Zürich*, *Werk: 1. 7 papers on modified Curtius Degradation.*
 2. Indicators

Naegli reported in an earlier paper, *Helv. 12, 206 (1929)*, that aliphatic isocyanates treated with aliphatic acids in a boiling benzene solution gave acylated amines, while, if the isocyanate was areomatic, diphenyl ureas were obtained along with the pure acid anhydride.

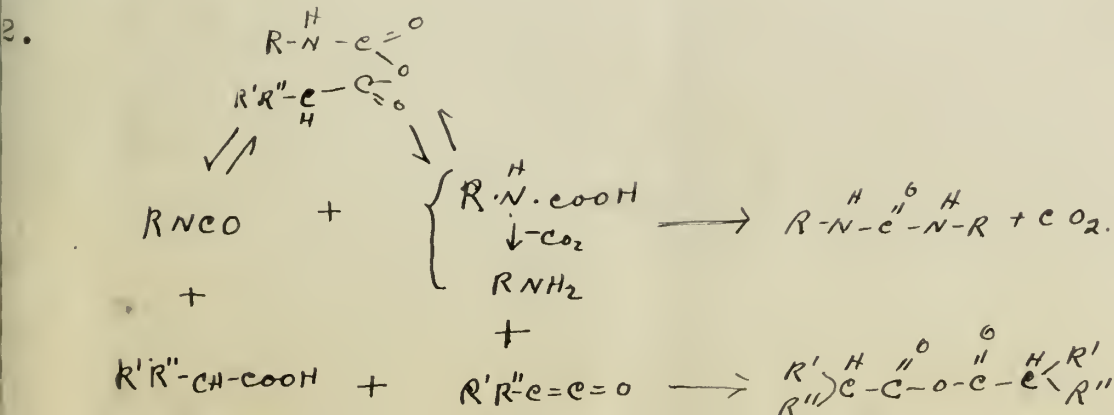
The arylisocyanate does not act as a true dehydrating agent on the acid, as SnCl_2 , P_2O_5 , etc., but reacts with the acid to form an intermediate product.

There are two mechanisms possible.



The reaction is in the direction of C in the case of aliphatic isocyanates and in the direction of D and E when the isocyanate is areomatic.

Naegli presents several analogies such as ketenes and acids to give anhydrides, etc.



These two mechanisms explain several reactions which until now had no explanation or else a false one. Some of these reactions are: 1) reaction of isocyanates and formanalide to give isonitriles and substituted ureas, 2) reaction of isonitriles on acids to give acid anhydrides and formanalide, 3) rearrangement of vinyl alcohol esters to the anhydrides and aldehydes. To establish in which direction the reaction actually proceeds, the mixed anhydride must be isolated and decomposed in the absence of excess ~~acid~~ acid or phenylisocyanate.

The action of phenylisocyanate on acids proceeds at low temperatures and is valuable for obtaining heat-sensitive anhydrides. The 3,5-dinitrophenylisocyanates increase the yields of the acid anhydrides.

I.

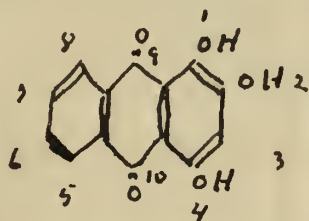
H. G. Kolloff

Structure of Boletol

Synthesis of Boletol and Isoboletol

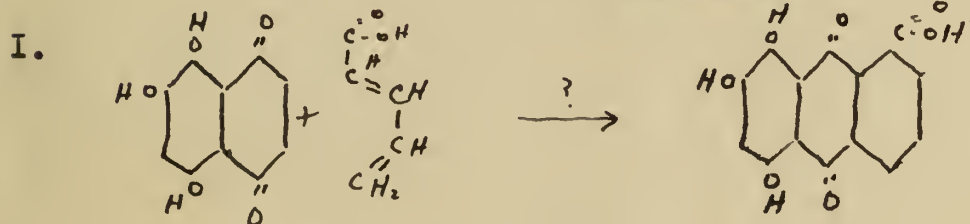
F. Kögl and W. B. Deizs Ann. 515 10,23 (1934)

Material from certain fungi which turns blue on exposure to air. Analyzed as $C_{15}H_8O_7$ gives triacetate $C_{21}H_{14}O_{10}$ with acetic anhydride. With zinc and acetic anhydride gives colorless pentacetate $C_{25}H_{20}O_{12}$. When treated with CH_2N_2 and then zinc and acetic anhydride a trimethyl leuco diacetate is obtained. When subjected to zinc dust distillation anthracene was obtained. On decarboxylation with soda lime the compound yielded purpurin. Hemi-mellitic acid resulted from oxidation of the original compound by hydrogen peroxide. Structure in view of reactions is

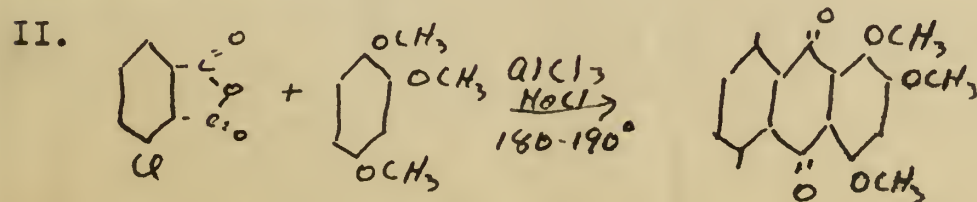


with COOH either in the 5 or 8 position.

II. Synthesis

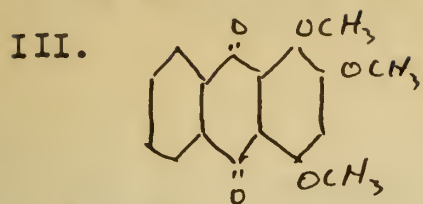


Reaction did not go.



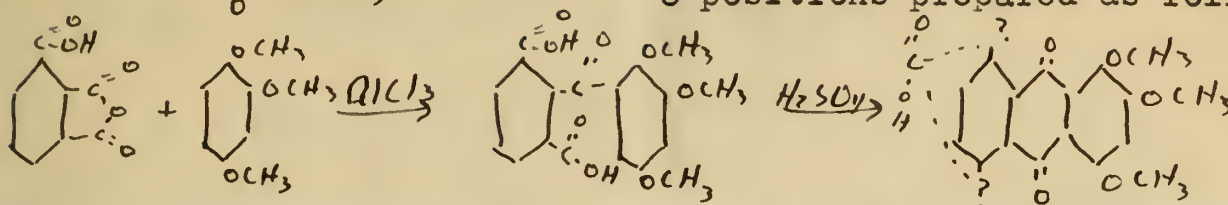
Mixture with Cl in 5 and 8 positions. Did not separate and go ~~through~~ cyanide

through cyanide.

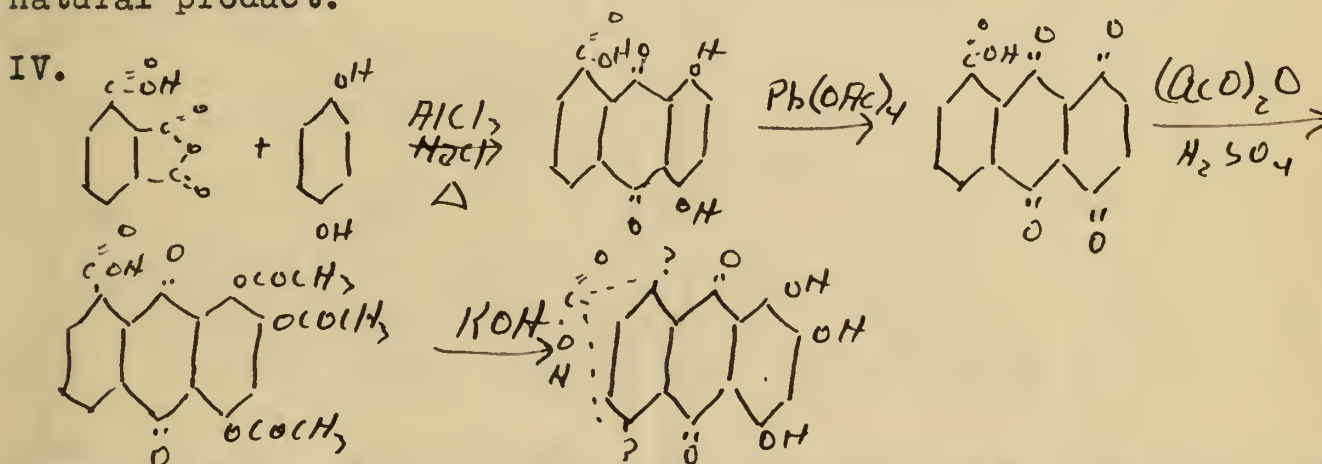


Mixture with carboxyl group in 5 and

8 positions prepared as follows:



Mixture separated and one of products when treated with zinc and acetic anhydride was identical with corresponding derivative of natural product.



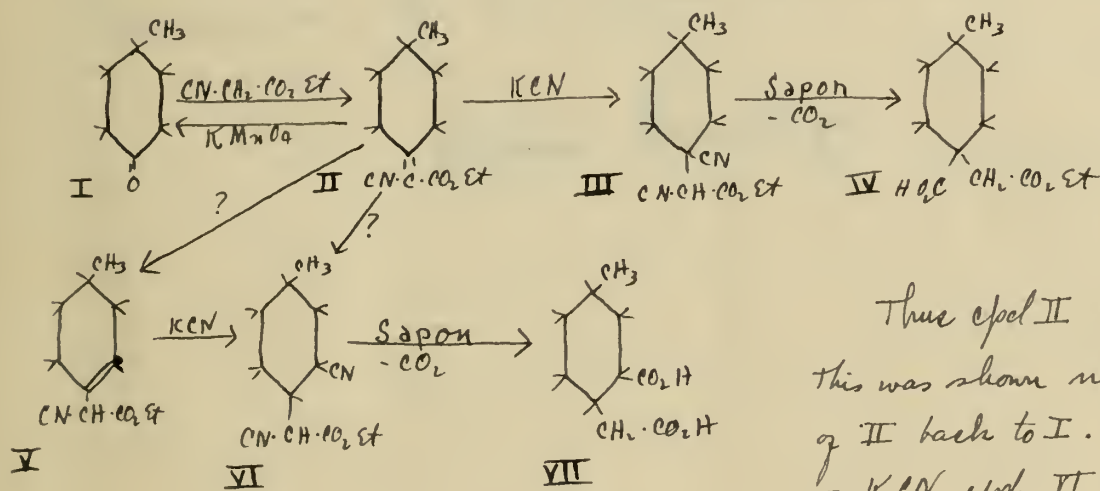
Mixture with COOH in 5 and 8 positions separated, one checks with natural product.

The Stereo isomerism of 4-methyl cyclo hepane, 1 acetic acid
1 carboxylic acid.

Stepan Goldschmidt & Gräfinger

Ber 68, 279 (1935)

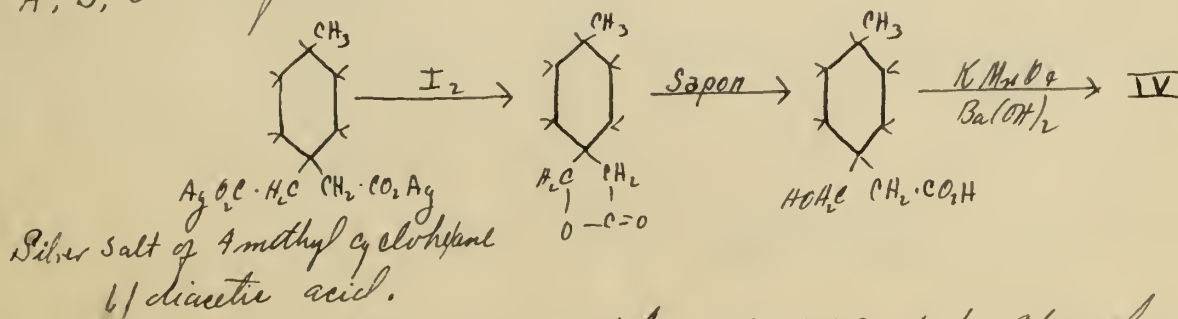
Goldschmidt, in checking over the work of Khuda [J. Ind. Chem Soc. 8, 277 (1931)]
the isolation of 4 stereoisomers of 4-methyl cyclohepane, 1 acetic acid, 1 carboxylic acid
and that during the course of the reaction that there was the possibility
present, that the 4 isomers were at least in part structure isomers.



Thus cpd II could rearrange into cpd V.
This was shown not to take place by oxidation
of II back to I. Also during the addition
of KCN cpd. II could be formed, and

finally the acid VII would be isolated and not IV.

Goldschmidt synthesized IV by another method & attempted to isolate
the acids A, B, C & D of Khuda.



Goldschmidt could not isolate acids B & D but obtained acids A & C pure.
He found that the melting point of a mixture of
1 mol A + 1 mol C corresponds to the M.P. of Khuda's acid D
4 mols A + 1 mol C " " " M.P. " " " B

Seminar

Feb. 6, 1935.

Conversion of Carboxylic Acids into Their Next
Higher Homologs.

W.O. Tutters —

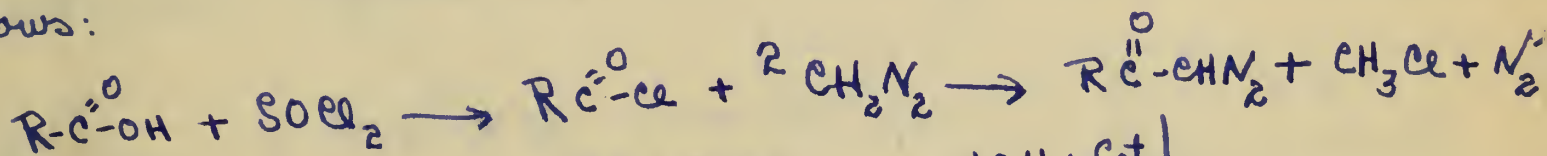
Conversion of Carboxylic Acids into their next higher homologs.F. Arndt and B. Eistert, Ber. 68, 200 (1935).

Univ. of Breslau

main lab. of I. G.

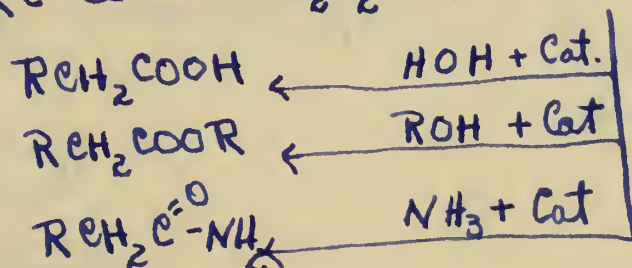
The methods available for conversion of a carboxylic acid into the next higher homolog are sometimes rather long, involving numerous steps, and also when certain groups such as ^{the} nitro or keto group are present in the molecule such a method can not be used.

The authors have developed a method whereby the acid containing one more carbon atom can be synthesized. This method involves only three steps, is quick, and produces the desired product in good yields. It can be represented as follows:



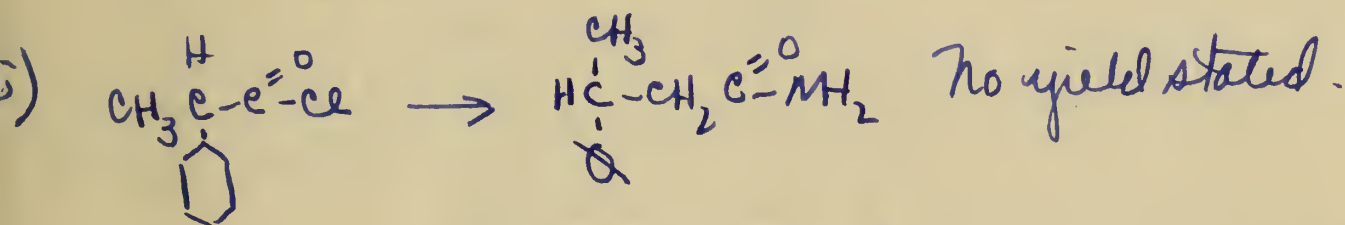
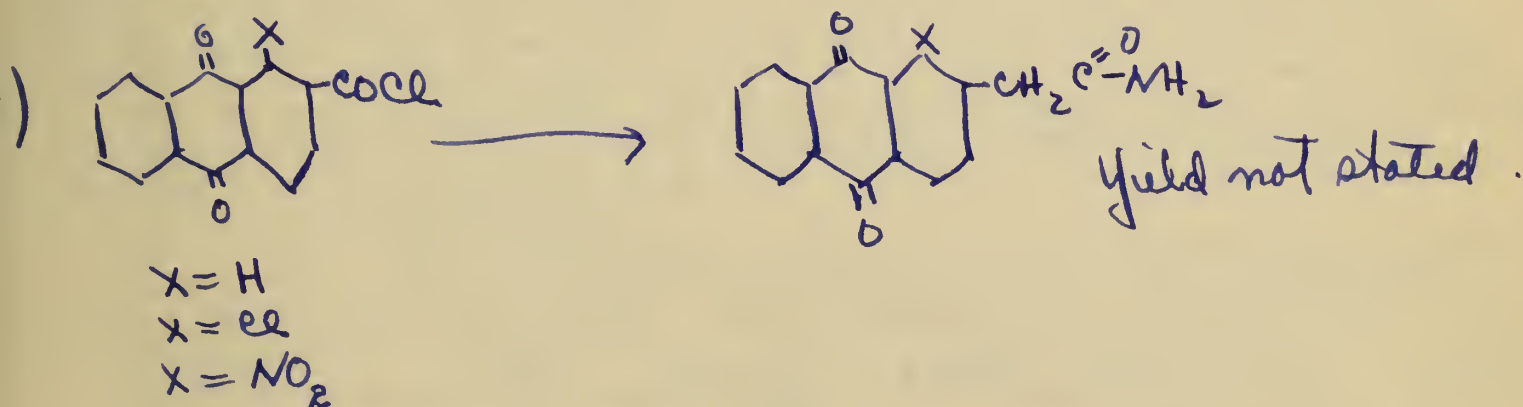
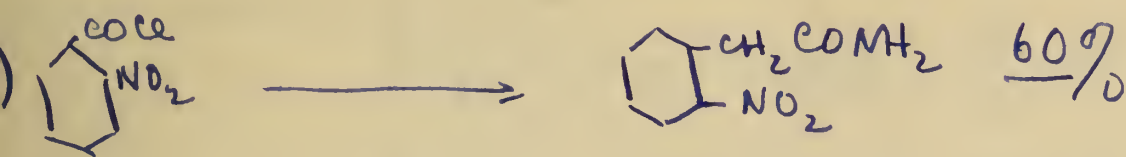
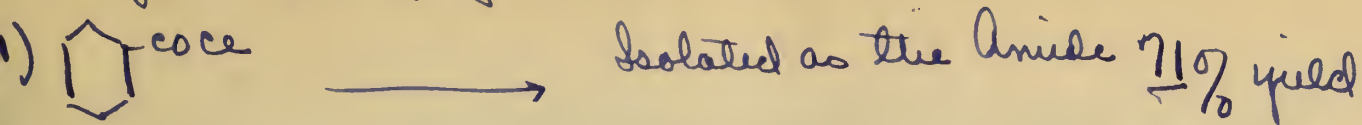
The catalyst can be one of the following:

Cu, Pt, Ag₂O, or colloidal Ag.

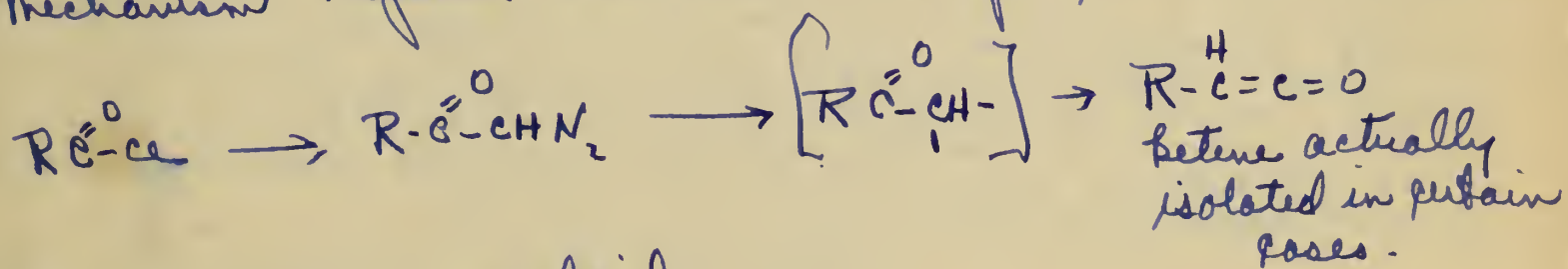


The authors state that the reaction goes the smoothest when the diazo-methyl ketone is rearranged in the presence of ammonia to give the amide which can be easily converted to the acid.

Some of the Cpd's prepared are as follows:



Mechanism Proposed is similar to one for Curtius Rearrangement



Ketene + Water \longrightarrow Acid

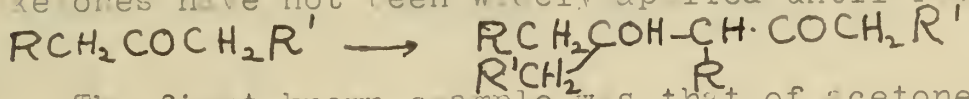
Ketene + Ammonia \longrightarrow Amide

Ketene + Alcohol \longrightarrow Ester

The Preparation of Ketols by Means of Fixed
Organo Magnesium Compounds

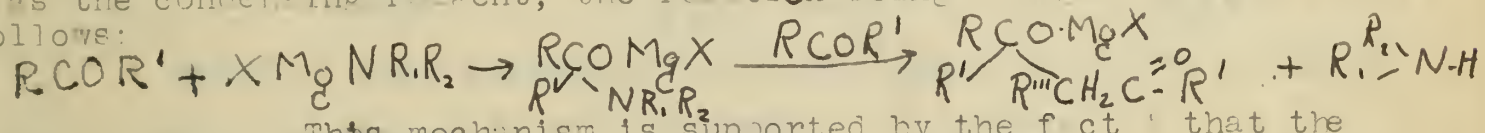
Colonge, J. comptes rendus 196 929 (1932)
Grignard, V. and Colonge, J. comptes rendus 196 1414 (1933)
Colonge, J. bull soc chim (5) 1 1101-1114 (1934)

The aldol condensation has long been known but similar reactions with ketones have not been widely applied until recently.



The first known example was that of acetone (R=H) in the presence of a strong alkali. Later it was applied to methyl ethyl ketone which gave a small yield of the ketol on long standing over alkali. Grignard and Fluchaire succeeded in isolating the ketols from a whole series of methyl ketones by use of $MgORX$ as a condensing agent. Finally Courtot and Cuperoff, still working with methyl ketones succeeded in getting them to condense with themselves by the use of aluminum chloride in the presence of alkylated aromatic amines $ArNR_2$. The yields in these reactions were poor.

In the present work the Grignard reagent prepared by treating a primary or secondary amine with an alkyl magnesium halide is used as the condensing reagent, the reaction being thought to take place as follows:



This mechanism is supported by the fact that the best yields are obtained by the use of one mol of $RMgX$ for every two mols of the ketone. Good yields are obtained if one of the R's in the amine is aromatic, but primary amines work just as well as secondary. Methyl aniline or aniline is usually used.

This reaction can be applied to other than methyl ketones, which is an important advance over the older methods. Higher ketones such as diethyl ketone and butyrene give only slightly smaller yield than the methyl ketones. Cyclic ketones can also be made to condense. In general all aliphatic ketones undergo this reaction if there exists on the carbon atoms immediately adjacent to the carbonyl a total of at least three atoms of hydrogen. Ketones such as benzophenone and fluorenone which by the above rule could not condense with themselves will nevertheless add the Grignard reagent as above and may then be allowed to react with other ketones to form mixed ketols.

The value of this work lies in the fact that it opens the way to the preparation of a whole series of compounds hitherto unobtainable by simple condensation methods.

M. Bowman

Zur Kenntnis der Perkinschen Synthese By Eugen Müller, Gawlick and Kreutzman.

II. Ann. 515 97 (1935)

I. Ann. 491 251 (1931)

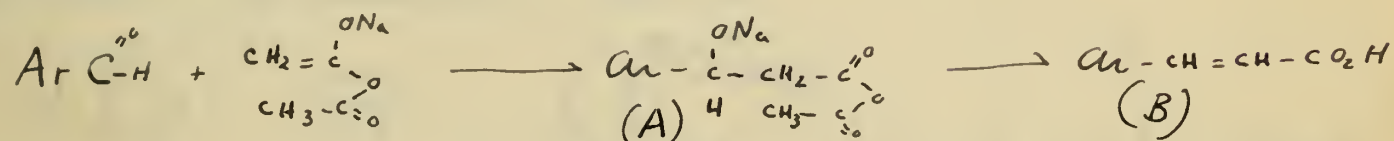
Review of Perkins Reaction. Kalnin, Helv. Chim. Act. 11 977 (1928)

Field (Müller) *Danzig*

Azobenzenes

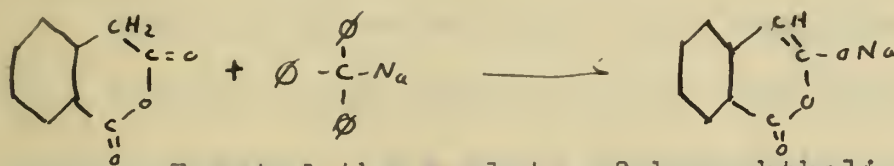
Sterols

Müller considers the Perkins Reaction a special case of the aldol condensation.

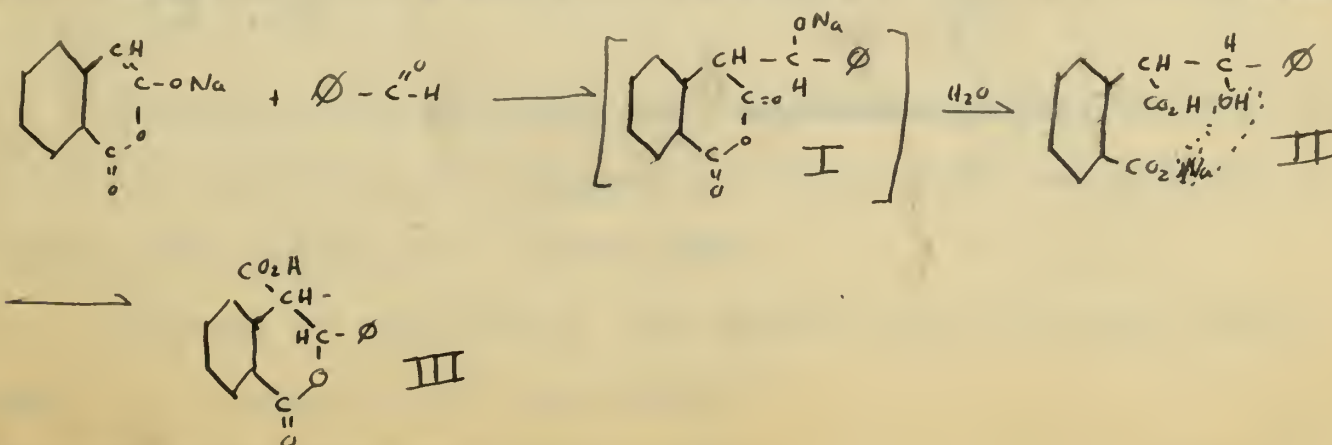


Proof of this mechanism would be indicated by the isolation of compounds analagous to (A) and (B).

Prepared the pure enolates, in almost quantitative yields, using triphenylmethyl sodium as the enolizing agent. Prepared the pure enolate of homophthalic anhydride



Treated the enolate of homophthalic anhydride with benzaldehyde, using no condensing agent. Did not isolate the anhydride (I), which is analagous to (A), but did isolate the hydroxy acid (II). More often the lactone (III) of the acid was obtained, in 85% yields.

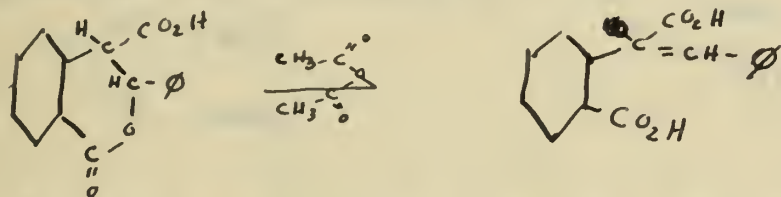


Proof of III

1. CH analysis $C_{16}H_{12}O_4$
2. Molecular weight determination
3. Neutral equivalent- for one carboxyl
4. Treatment with diazomethane, and determination of Zeisel number showed one OCH_3
5. Compound III not identical with benzal homophthalic ^{acid} anhydride (IV)

On treatment of III with acetic anhydride obtained benzalhomophthalic ^{acid} anhydride (IV) which is analagous to (B).

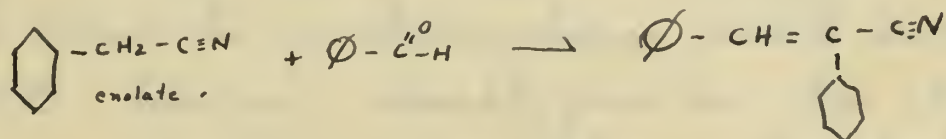
Thus compounds analagous to both (A) and (B) are indicated, and proof of the mechanism is possible.



To show mechanism was general, used o-nitrobenzaldehyde, o-methoxybenzaldehyde, and p-dimethylaminobenzaldehyde. Obtained yields of lactones analagous to (III) of 83%, 55% and 17% respectively.

Reaction of benzaldehyde with enolates of succinic anhydride, ethyl acetate, ethyl phenylacetate, and benzyl cyanide, without condensing agent, gave small yields of the expected α - β unsaturated compound.

Example.



Reaction of benzaldehyde with ~~enolates~~ enolates of compounds containing one hydrogen on α -C atom did not proceed, as is the case in the aldol condensation.

Contrary to expectations, the sodium salt of malonic ester would not condense with benzaldehyde.

Extension of the Michael's Reaction

Ghosh & Guha

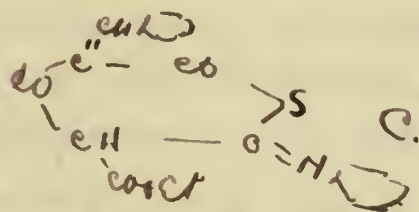
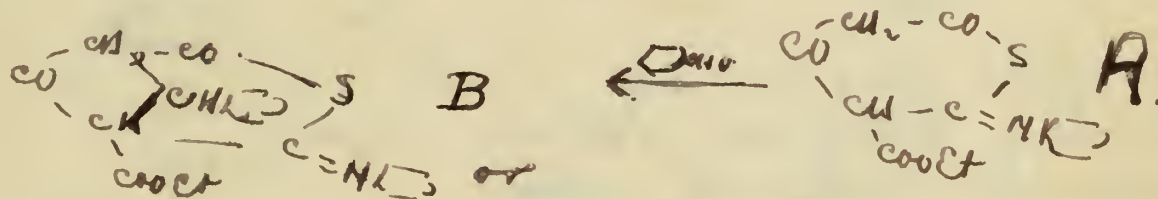
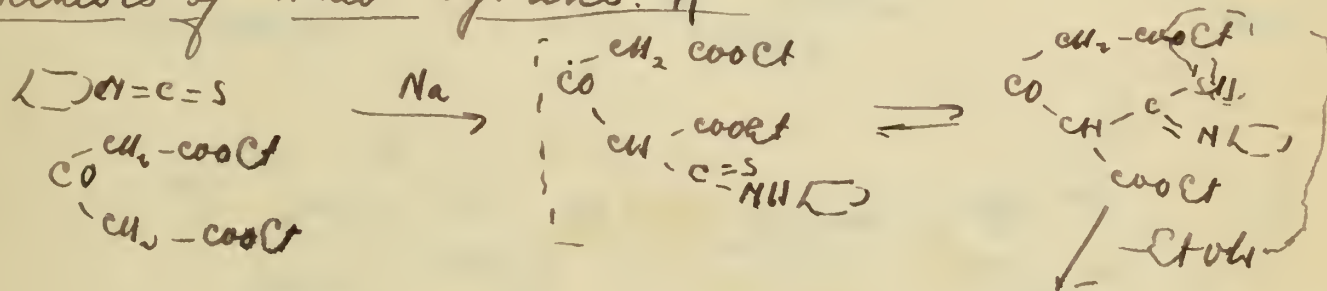
J. Ind. Chem. Soc. XI, 353, (1934)

Ethyl carbamate is substituted for the active methylene groups in the condensation.

Phenyl isocyanate and Phenyl is-thio^{cyanat} are used as the unsaturated component of the reaction



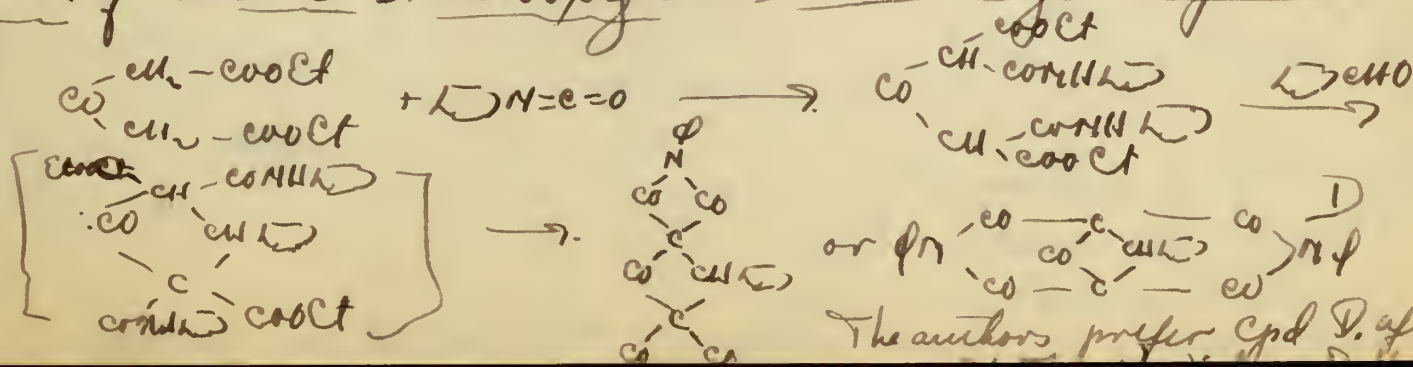
Synthesis of Thio Pyrans. A



Cpd B is prepared by the authors, as Cpd A gives a di-sodium deriv. while the spd. resulting from it gives no

Na derivative. Cpd B thus enolization would form double bond and C atom involved in the bridge and hence be in discordance with Bredt's Rule.

Cpd C however should give a Na derivative cond. of acetone Dicarboxylate with Phenyl isocyanate



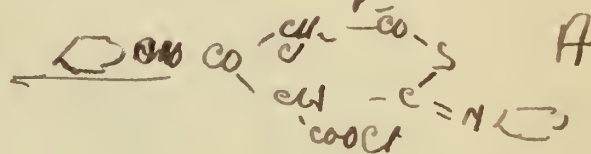
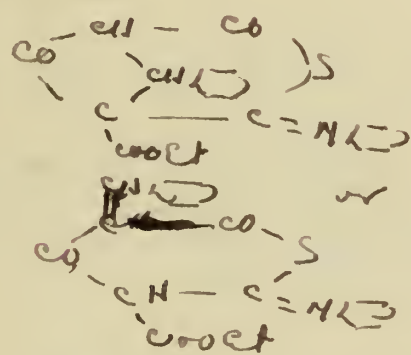
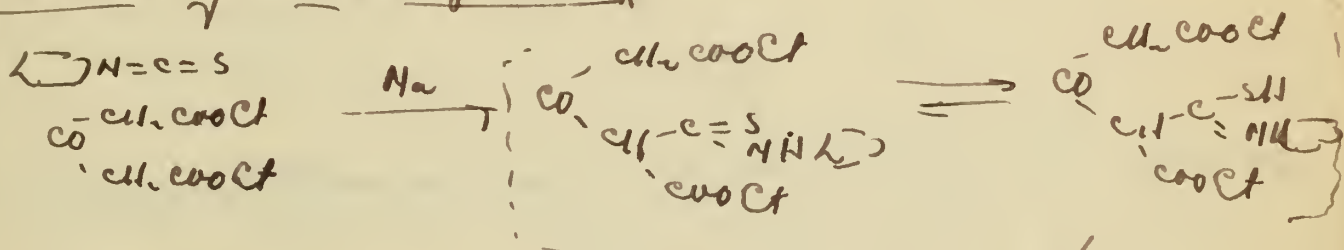
The authors prefer Cpd D.

Ethyl carbamate is substituted for the active methylene
cpd in the Michael's condensation

Phenyl isocyanate and phenyl thiocyanate are used as
the unsaturated component of the reaction

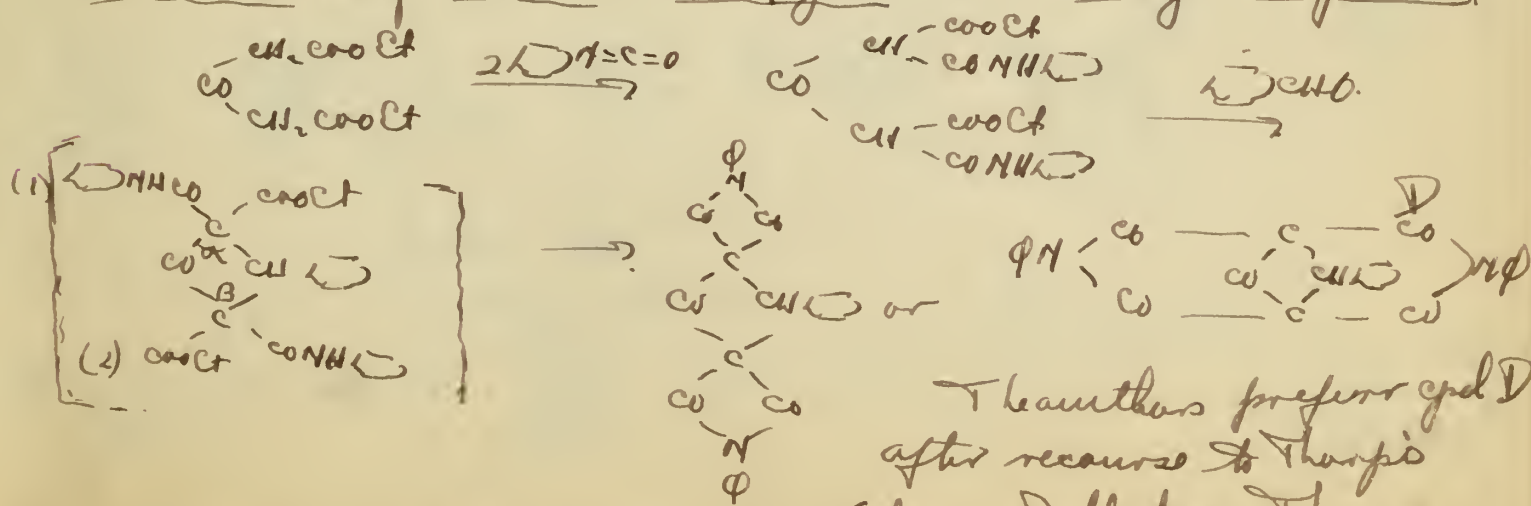


Synthesis of Thio Pyrans A.



Cpd B is preferred by the
authors as Cpd A gives a di-
sodium derivative, while the cpd
resulting from its condensation with benzaldehyde
gives no Na derivative. Cpd B through enolization
would form a double bond on C atom involved in
the bridge, and hence be in discordance with Bredt's
Rule. Cpd. C, however should give a Na derivative

Condensation of Acetone Dicarboxylate with Phenyl isocyanate



The authors prefer cpd D
after recourse to Thorpe's
Valency Deflection Theory.

decrease in angles α & β result in incidence of angle about

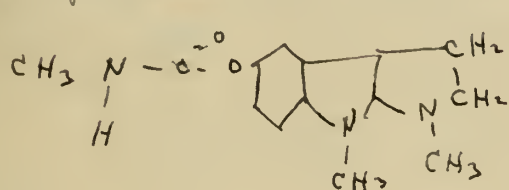
Synthetic Studies on Carine (physostigmine)

A) Ann 500 42 (1932) Hoshino and Katsuka
 " 516 76 (1935)
 " " 81 (1935)

B) J. A. C. S, 56, 1796, (1934) Julian and Pihl
 " 57 539 (1935) " "
 " " 563 " " "
 " " 755 " " "

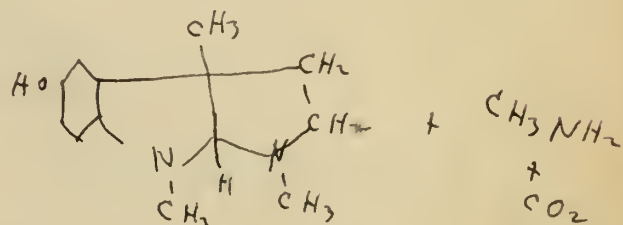
from the organic chemical division of the Technical University of
 Tokyo - Yokoyama.

① Proposed formula for Carine



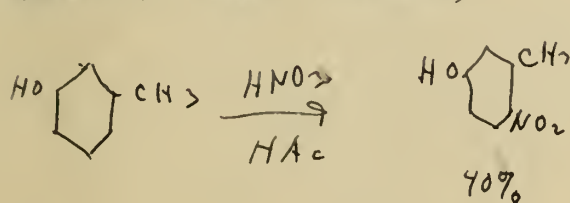
Carine.

alk

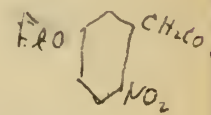
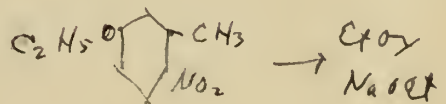
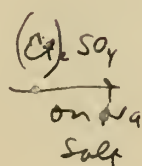


Esroline

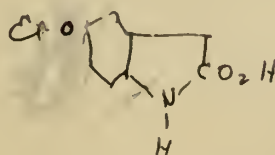
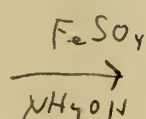
② Hoshino's work. (Ref A)



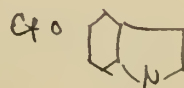
40%



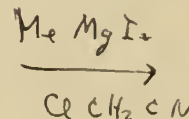
5 ethoxy 2 nitro
 phenyl
 pyruvic acid



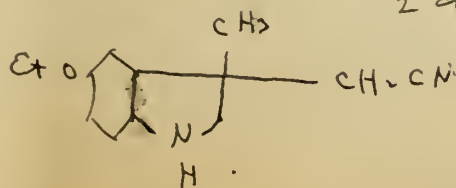
210°



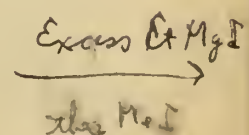
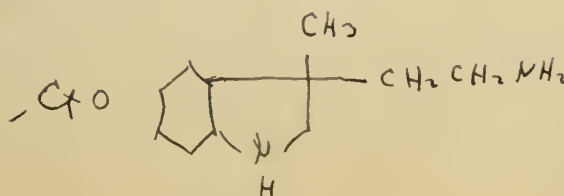
75%

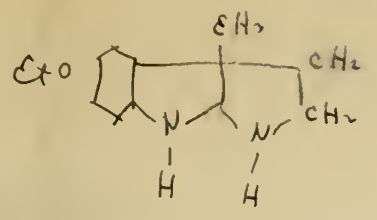


5 ethoxy indol
 2 carboxylic acid

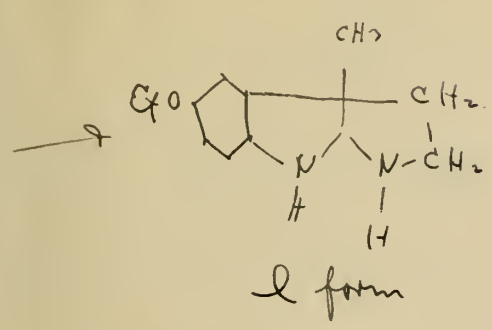


30%

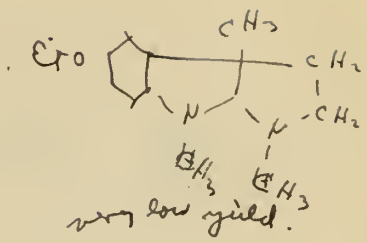
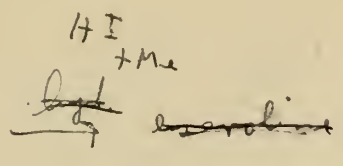




resolved using
d tartaric acid
and Brom camphor sulfonic acid

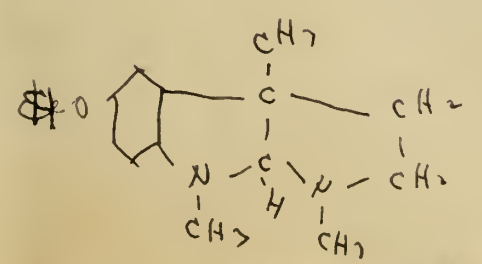
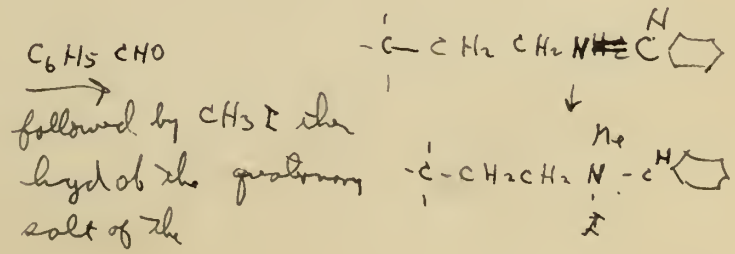
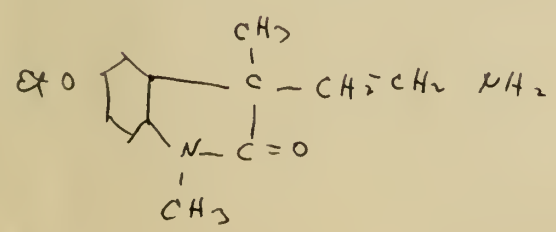
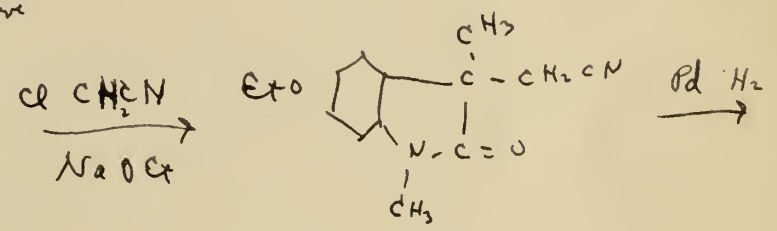
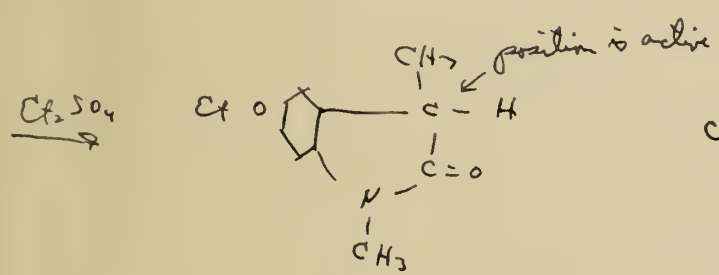
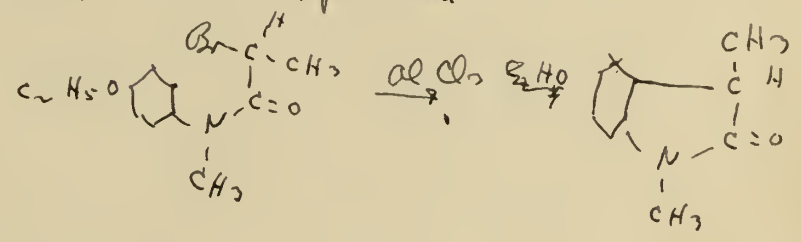
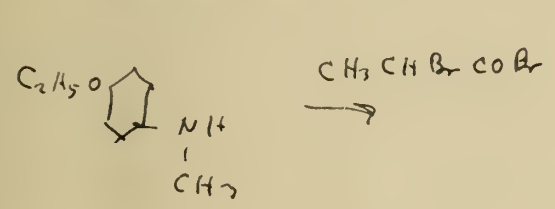


+ d form

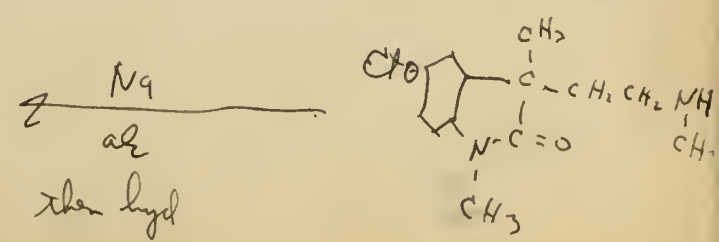


↓ hyd.
Eservoline l form identical
with that from natural sources
also all derivatives identical.

③ Julian has substantiated the Japanese authors (Ref B)
showed oxindols to be reactive in the 3 position.



85-90
all eservoline



d l asaroline $\xrightarrow[\text{resolution}]{\text{d tartaric}}$ l asaroline identical with that of the Japanese authors
and with the natural product.

l asaroline + CH_3CNO l asarine also identical with natural product.
methyl
isocyanate

a better method of resolution was to resolve the amine before ring closure.

H. S. Schreiber 25

The Influence of Acid, Ester & Nitrile Groups on Intramolecular Transformations of the Allyl Type - I, II, III

Ramond Bull. Soc. Chim. 153 1206, 1318, 1342 69.

The author has studied the effects of acid ester and nitrile groups on a molecule of the following type $\text{RCH}_2=\text{CH}-\underset{\text{X}}{\text{CH}}-\text{R}$ where $\text{R} = \text{COOH}, \text{COOR}, \text{or CN}$ and $\text{X} = \text{Cl}, \text{Br}, \text{OH} + \text{OEOCH}_3$. His starting material is vinyl α hydroxyacetonitrile which is prepared as follows

$$\text{CH}_2=\text{CH}-\text{CHO} + \text{KCN} + \text{CH}_3\text{COOH} \rightarrow \text{CH}_2=\text{CH}-\underset{\text{OH}}{\text{CH}}-\text{CN} + \text{CH}_3\text{COOK}$$

70-77% yield

The acid & ester groups are produced by hydrolysis and esterification of the cyanohydrin respectively. The hydroxyl group is then replaced by $\text{Cl}, \text{Br} + \text{OEOCH}_3$ and these derivatives treated with various reagents to see whether or not a rearrangement takes place. The author classifies the type of reactions into three groups.

- (A) Normal reactions - ones in which the X group has merely been replaced by another as Y .
- (B) Anionotropic reactions - ones in which the X group has been replaced by Y with a shift to the δ position from the α and a corresponding shift of the double bond.
- (C) Prototropic reactions - ones in which the X group is not replaced, but instead a hydrogen atom shifts from the α to δ position with a corresponding shift of the double bond.

26

The author arrives at three general conclusions from his work.

- I. The introduction of an acid, ester or nitrile group tends to prevent any rearrangement, $\alpha \rightarrow \gamma$, altho rearrangement takes place it is not as readily as in the corresponding hydrocarbon.
- II The introduction of an acid ~~ester~~, or nitrile group prevents any of the reverse rearrangement $\gamma \rightarrow \alpha$.
- III The introduction of an acid, ester or nitrile group promotes the shift of a hydrogen atom rather than a negative group as OH, Cl, COCH₃, etc. especially in basic solutions.

son isolated ^{from coal tar} (a) golden-orange hydrocarbon, which he concluded consisted of one or more naphthalene homologues. No homologues of naphthalene had previously been synthesized so he started out with the synthesis of 2,6-dimethylnaphthalene, which he felt quite certain was the main constituent of his colored material. He accomplished the synthesis by three methods:

CH₃ very poor yield

m.p. 365°

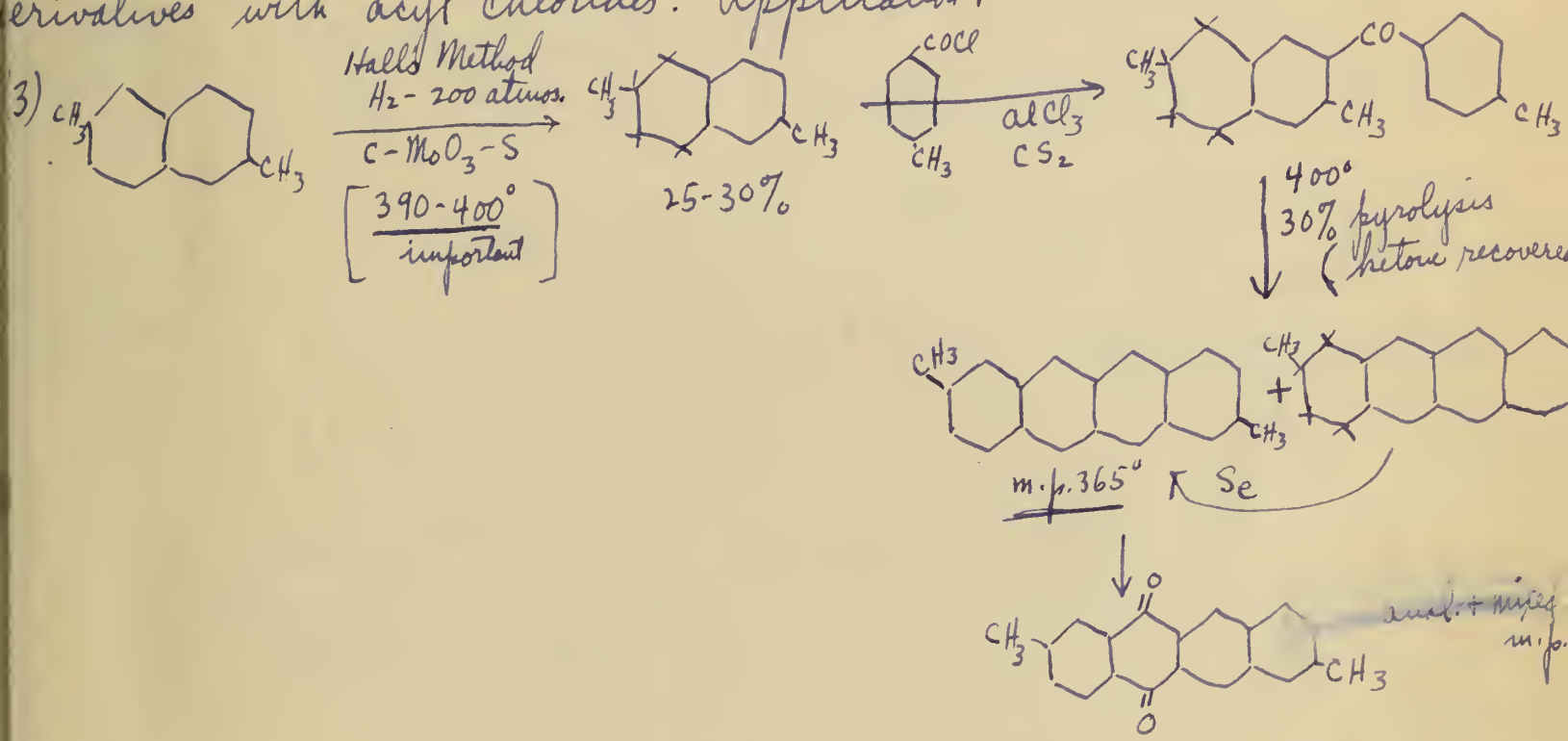
Pyrolysis of 3-p-toluenyl-2,6-dimethylnaphthalene

98% H_2SO_4 $\xrightarrow{135^\circ}$ CC1=CC=C(C(=C2C=CC(=C(C)C)C=C2C)C)C $\xrightarrow[\text{w. alk. (fusion)}]{\Delta \text{ Na salt}}$ CC1=CC=C(C(=C2C=CC(=C(C)C)C=C2C)O)C 40% $\xrightarrow[\text{(Bucherer React.)}]{(\text{NH}_4)_2\text{SO}_3 + \text{NH}_4\text{OH, autoclave}}$ CC1=CC=C(C(=C2C=CC(=C(C)C)C=C2C)N)C 80% $\xrightarrow[\text{K Cu(CN)}]{\text{HCl, NaNO}_2}$ CC1=CC=C(C(=C2C=CC(=C(C)C)C=C2C)C#N)C

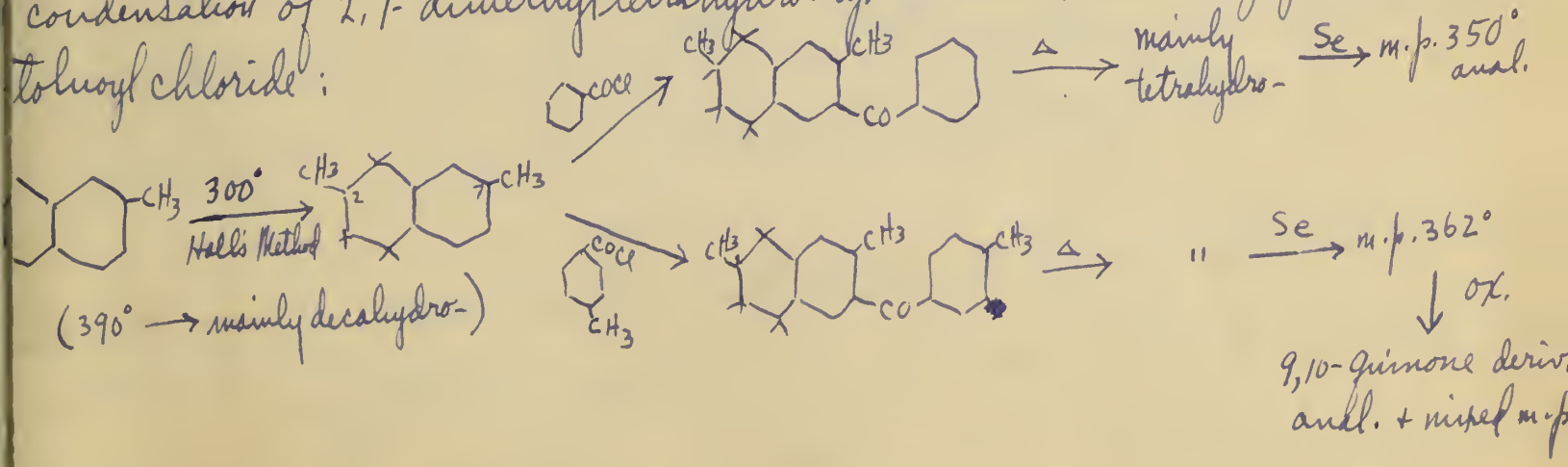
CC1=CC=C(C(=C2C=CC(=C(C)C)C=C2C)C(=O)OC3=CC=C(C)C=C3)C 43% $\xrightarrow[\text{alcl}_3]{\text{cyclohexyl methyl ether}}$ CC1=CC=C(C(=C2C=CC(=C(C)C)C=C2C)C(=O)Cl)C $\xrightarrow[3 \text{ hrs.}]{\text{SOCl}_2}$ CC1=CC=C(C(=C2C=CC(=C(C)C)C=C2C)C(=O)O)C 62% from base $\xrightarrow[24 \text{ hrs.}]{5\% \text{ aq. KOH}}$ CC1=CC=C(C(=C2C=CC(=C(C)C)C=C2C)C#N)C

CC1=CC=C(C(=C2C=CC(=C(C)C)C=C2C)C(=O)OC3=CC=C(C)C=C3)C $\xrightarrow[4 \text{ hrs.}]{360-400^\circ}$ CC1=CC=C(C(=C2C=CC(=C(C)C)C=C2C)C(=O)OC3=CC=C(C)C=C3)C + CC1=CC=C(C(=C2C=CC(=C(C)C)C=C2C)C(=O)OC3=CC=C(C)C=C3)C $\xrightarrow[\text{H OAc}]{\text{CrO}_3}$ 2,6-dimethylnaphthalene-9,10-quinone

In attempting to prepare 2,7-dimethylnaphthacene by a condensation of 3,6-dimethyl-2-naphthoyl chloride, there was obtained ill-defined and resinous products. The problem was solved by separation and use in the Friedel-Crafts' condensation of the tetrahydro derivatives of 2,6- and 2,7-dimethylnaphthalenes. These tetrahydro derivatives reacted as smoothly and quantitatively as benzene derivatives with acyl chlorides. Application:

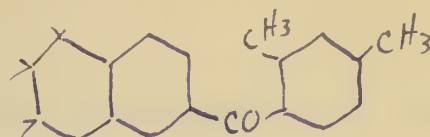
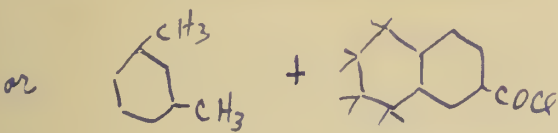
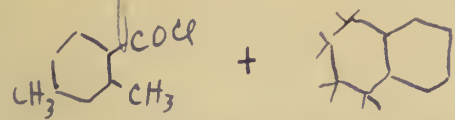


thesis of 2-methyl- and 2,7-dimethylnaphthacenes were prepared similar condensation of 2,7-dimethyl-tetrahydronaphthalene with benzoyl^{chloride} and with toluoyl chloride:



Condensation Synthesis for 2-methylnaphthacene

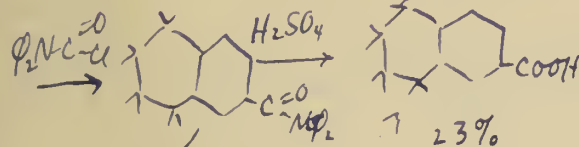
condensation of either



93%

96%

400° + unchanged ketone
repyrolyzed till 30%
conversion was obtained



↑ 3 SOCl₂

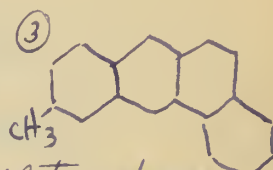
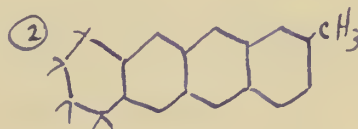
23%

mixture of 3 cpds from 50 gr. of ketone

proof for this
condensation

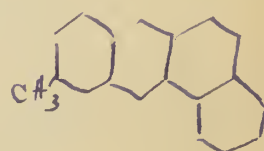
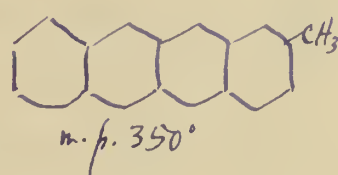


.2 gr.
m.p. 350°



15 gr. unable to separate

↓ Se (good yield obtained)



↓ ox.
corresp. quinone

resin, probably
mixture of 9,10- and
11,12-quinones of 2-methylnaphthacene

other methods have been presented for the synthesis of naphthacene homologues, cpds not previously synthesized.

extension of the Friedel Crafts' condensation of tetrahydro derivatives of naphthalene (or substituted naphthalenes) with acyl chlorides should prove valuable in the synthesis of certain, more important compounds than the naphthacene homologues.

Seminar Abstract

Reciprocal Transpositions of Phenylacetylcarbinol and Benzoylmethylcarbinol- a New Type of Tautomerism.

A. E. Favorsky and T. I. Tewnikowa, Bull. Soc. Chim. (5), 2, 253-73, (1935).

Neuberg and Ohle, and Auwers and Mauss found that

$\text{C}_6\text{H}_5\text{COCH(OH)CH}_3 \rightleftharpoons \text{C}_6\text{H}_5\text{CH(OH)CH}_2\text{COCH}_3$ gave the same products with semicarbazide, thiosemicarbazide, and phenyl isocyanate. The authors found that with benzoyl chloride both gave mixtures of benzoates and with CH_3MgBr both gave a mixture of glycols. With $\text{C}_6\text{H}_5\text{MgBr}$ the first gave a mixture of glycols while the second gave $\text{C}_6\text{H}_5\text{-CH(OH)-CH}_2\text{-CH}_2\text{-C}_6\text{H}_5$. Thus the two carbinols are chemical individualities

which do not rearrange by themselves. There takes place a new type of tautomerism in their reactions, like keto-enolic; this is keto-anolic or keto-carbinolic. There takes place a migration of two atoms of hydrogen.



March 10, 1955
31

ORGANIC SEMINAR

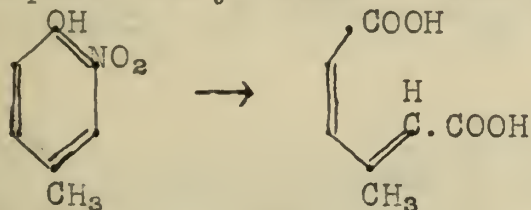
Ring Cleavage of o-nitro Phenols by H₂SO₄. I

by O. Neunhoeffer and H. Kölbel

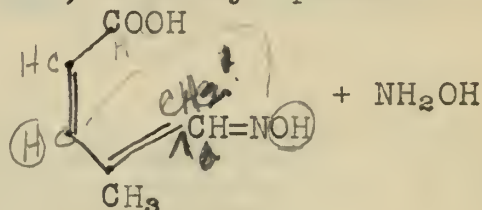
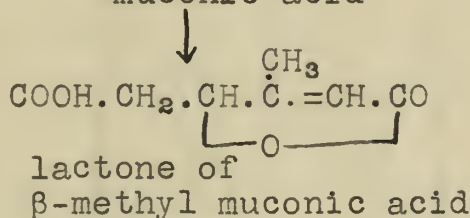
Chem. Inst. Univ. Greifswald

Reference: Ber. 68 620 (1935)

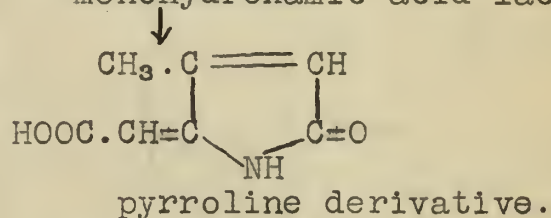
The reaction of concentrated or fuming sulfuric acid with the para substituted, o-nitrophenols (1) 2,4-dimethyl 6-nitrophenol, (2) 2,4-dibromo 6-nitrophenol and (3) 1-nitro-2-naphthol, results in ring cleavage with the formation of (A) the lactones of the substituted muconic acids, (B) the substituted mucomonohydroxamic acids, (C) the pyrroline derivatives resulting from (B) by loss of H₂O or (D) a mixture of (A)-(B). These products are analogous to those previously found in the case of 2-nitro, 4-methyl phenol.



2-nitro 4-methyl phenol β-methyl muconic acid



β-methyl muco-monohydroxamic acid lactone



In the case of the 2,4-dibromo 6-nitrophenol, the lactone formed had a bright red color, for which the author gave the possible explanation of tautomerism to a hydroxyfurane form.

The mechanism of the reaction was studied, but not determined. Experimental results indicated that an intermediate H₂SO₄ derivative was formed, which on hydrolysis produced the products which were observed.

Meredith Sparks

The addition of Sulfur Dioxide to Olefines.

by Standinger and Ritzenthaler, Ber., 68B, 455 (1935)

Standinger ~~is~~ located at the U. of Freiburg and is noted mainly for his work on polymerization.

The results of Standinger's work may be recorded as follows:

Olefine	Without Catalyst		with - catalyst		with + catalyst		n	mol. wt.
	monomer	Polymer	monomer	Polymer	monomer	Polymer		
Ethylene						100%		
Propylene 13.4		13g.				100%	3700	390,000
Butadiene 15.4	10g.	13g	30%			60%	1300	106,000
Isoprene 15.4	2.7g.	17g.	16g.	3g.	0g.	12%	1000	135,000
Dimethyl Butadiene 25.4	21g.	8.8g.	27g.	0g		21%	840	120,000

The following conclusions can also be observed:

1. Dimethyl butadiene > Isoprene > Butadiene in % yield monomer
" < " < " in % " polymer
2. An increase in the number of moles of SO_2 per mole of olefine causes an increase in the percentage yield of monomer and a decrease in % yield of polymer.
3. The larger the amount of anticatalyst used causes an increase in the % yield of butadiene monomer.

Reported by

J. C. Eck

The first part of the paper is devoted to a general discussion of the problem. It is shown that the problem is of great importance in the theory of the structure of the atom. The second part is devoted to a detailed discussion of the problem. It is shown that the problem is of great importance in the theory of the structure of the atom.

Date	Time	Place	Subject	Remarks	Signature	Date

The third part of the paper is devoted to a detailed discussion of the problem. It is shown that the problem is of great importance in the theory of the structure of the atom. The fourth part is devoted to a detailed discussion of the problem. It is shown that the problem is of great importance in the theory of the structure of the atom.

The Synthesis of Jasmonone

J. R. Little 33
May 1, 1935

H. Treff and H. Werner: Ber. 68, 640 (1935).
" " " Ber. 66, 1521 (1933).

Ruzicka and Pfeiffer: Helv. 16, 1208 (1933)

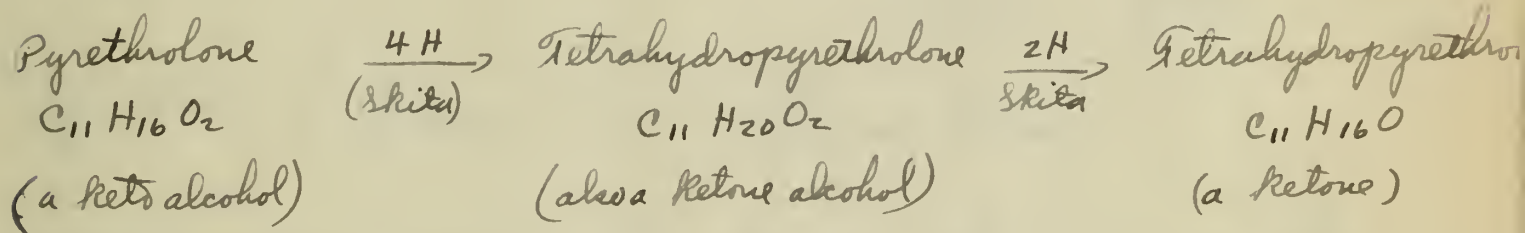
Staudinger and Ruzicka: Helv. 7, 212, 236, 245 (1924).

Treff located at Chem. Lab of Heine & Co., Leipzig and Gröba.

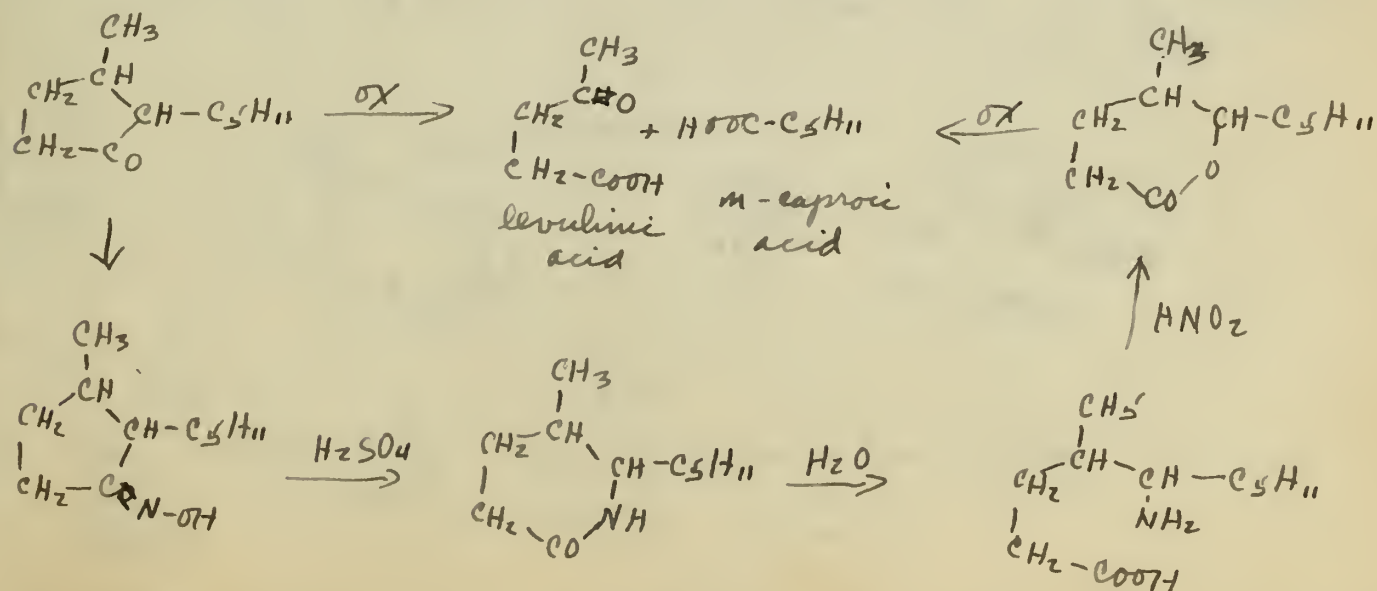
Werner located at Univ. of Hamburg. Work mostly with Schmalz.

Jasmonone discovered in 1899 by Hesse and composition determined as $C_{11}H_{16}O$.

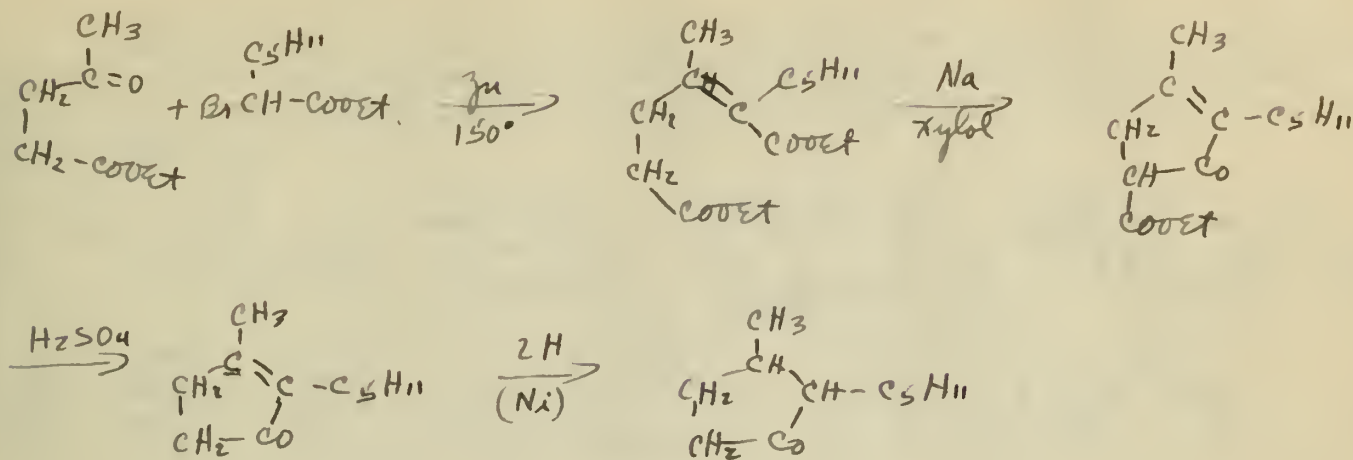
Jasmonone has same carbon skeleton as pyrethrolone which was determined by Staudinger and Ruzicka in 1924.



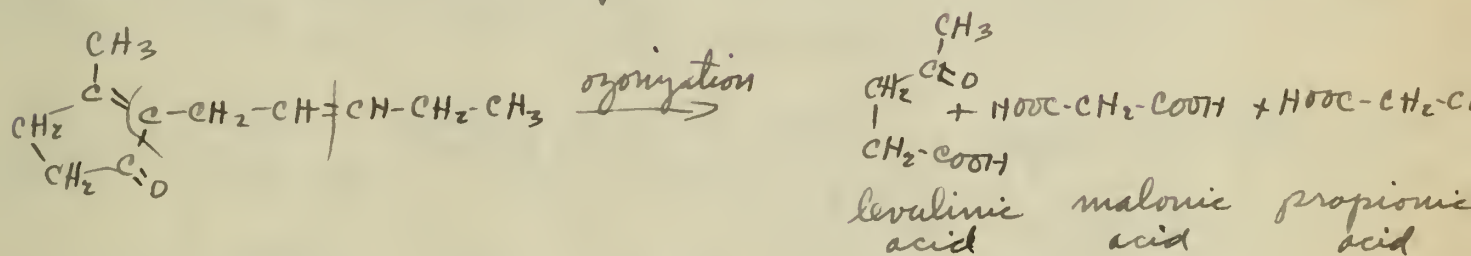
Tetrahydropyrethron later found identical with tetrahydrojasmonone structure shown by:



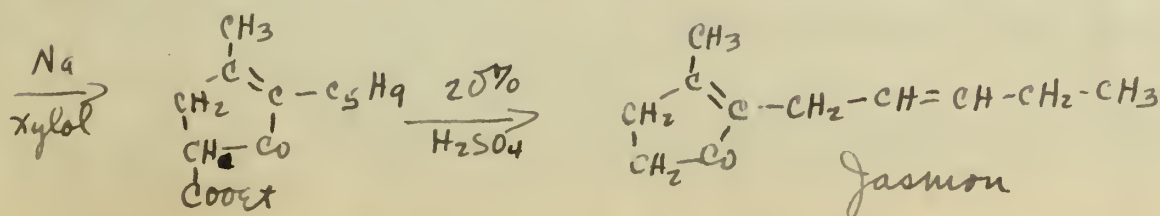
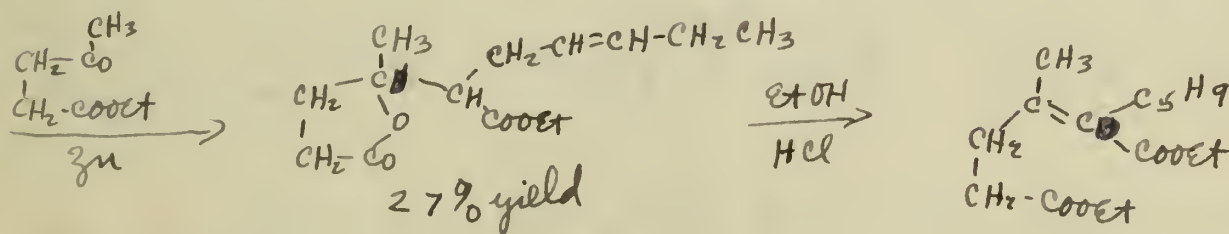
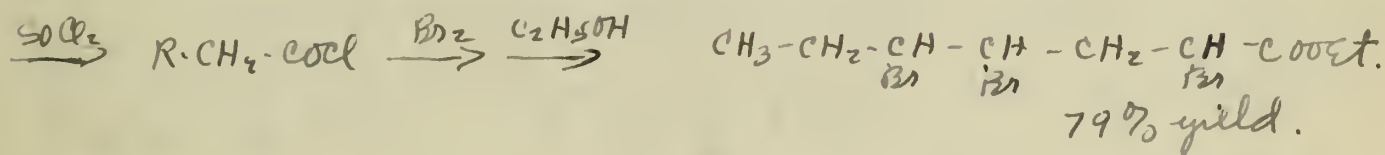
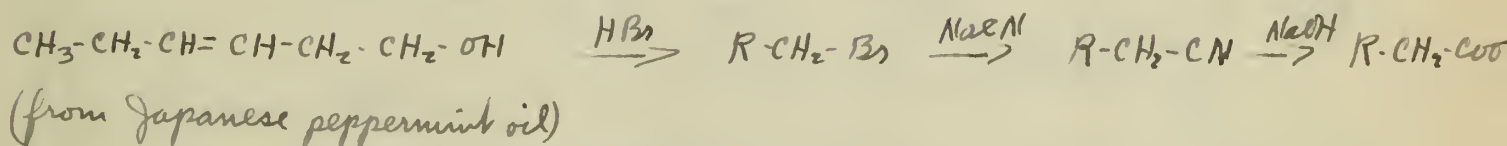
Tetrahydropyrene synthesized as further proof of structure.



Tetrahydrojasmon found to be identical with tetrahydropyrene.
Double bonds located by:



Synthesis of Jasmon by Treff and Werner.



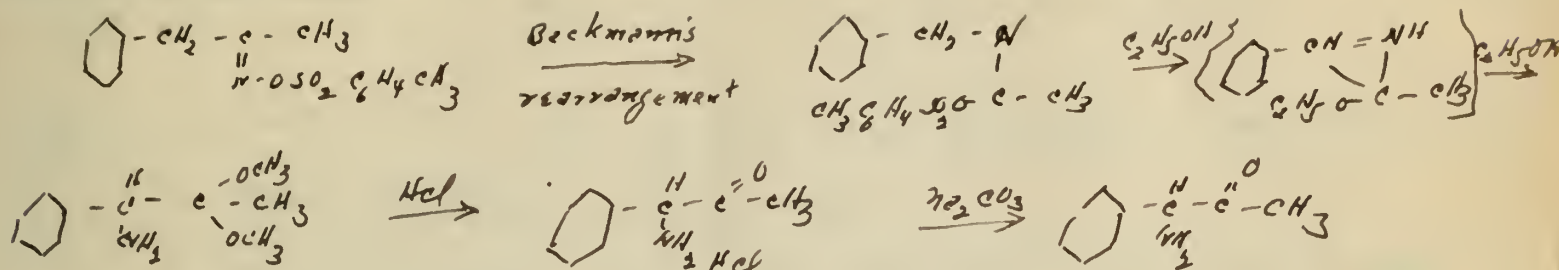
Synthetic product found to be identical with natural product.

P. W. NEBER and GINGANG HUN

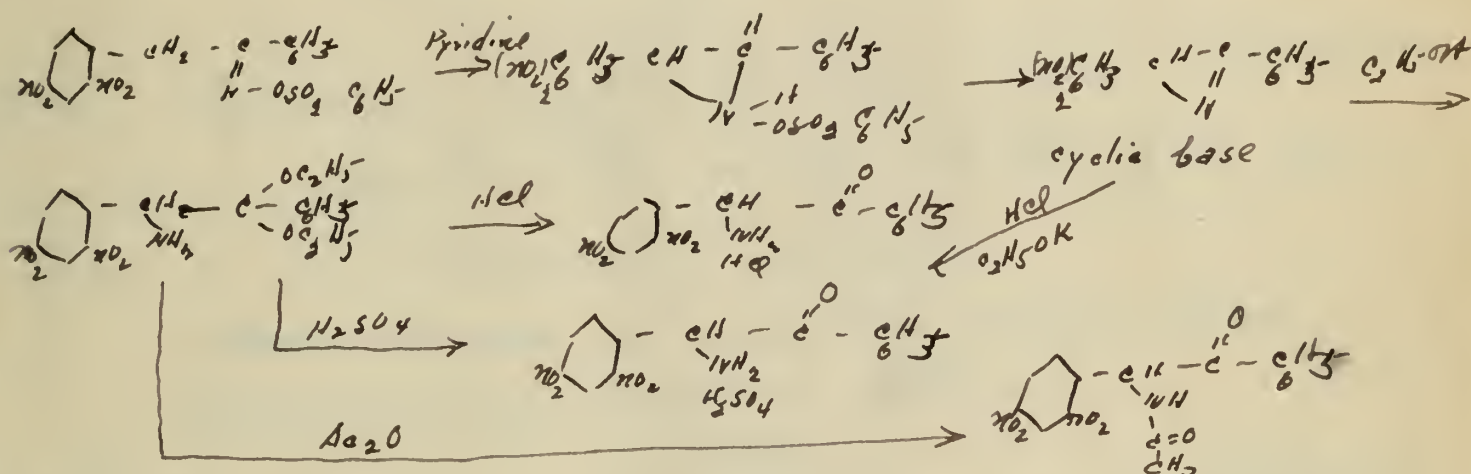
Ann, 515, p. 283 1935.

Handwritten signature: H. W. Neber

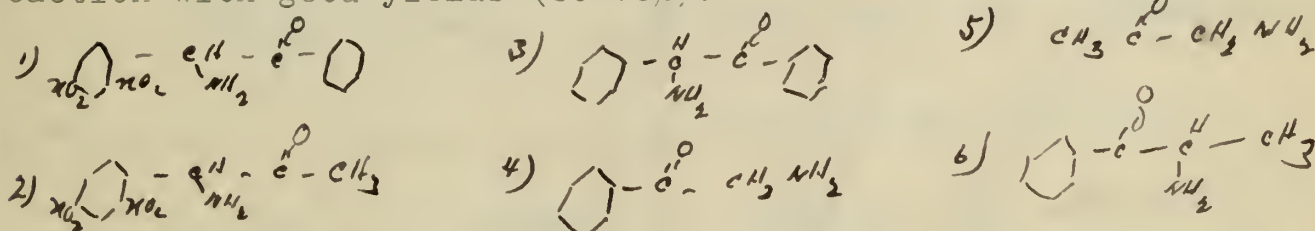
Neber obtained an acetal by treating benzyl-methyl-ketoxime p-toluolsulfoester with potassium ethoxide and acetic acid. The acetal on hydrolysis gave an α amino ketone. The first mechanism indicated by the author is as follows:



In a later research, the author obtained a cyclic base from 2,4 dinitro, benzyl methyl ketoxime. When the cyclic base was treated with potassium methoxide and hydrochloric acid, it yielded an α amino ketone salt. It proved that the first proposed mechanism was wrong.



A series of α amino ketones have been prepared by means of this reaction with good yields (65-75%).



This reaction can be used as a general method for making α amino ketone provided that

- 1) The starting ketoxime is derived from a ketone which contains this grouping ($-\text{CH}_2-\text{C}(\text{O})-$).
- 2) The ketones must be transferred to the p-toluolsulfoester in the first step, otherwise they do not undergo the desired reactions, as shown by the authors working with esters of another nature.

The Amid Group, Hydroxamic, Sulfinic, and Sulfhydroxamic Acids,

The Nitro Group and the Nitronic Esters.

Report by W. C. Ashley

Fritz Arndt and J. D. Rose, II, Ann., 510, 62 (1934); III, J. C. S., 1 (1935).

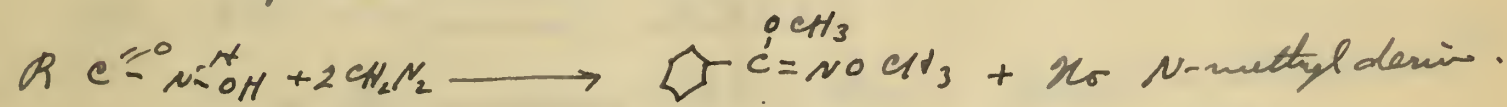
Published since 1911 (Uni. of Kiel, Uni. of Breslau, Oxford Univ. now).

- Various sulfur compounds.
- Cyclic azoxy compounds; aliphatic azo compounds.
- Triazines and triazoles.
- Dipyrenes and dipyrylium salts, fulvene.
- Syntheses with diazomethane.

Part II: Saccharin reacts with CH_2N_2 to give an N-methyl and a O-methyl derivative or only N-methyl if the Kpd. is added to the diazomethane solution.

Phalimid does not react with diazomethane.

Hydroxamic acid reacts as follows:

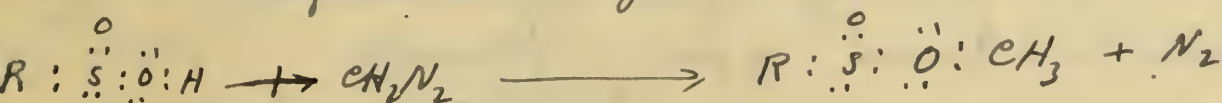


Sulfhydroxamic acid gives an N-methyl deriv.



clearly indicating a difference between the structures of SO_2 and $=\text{C}$

Sulfuric acid gives no sulfone but all sulfinic ester



III. Nitro-Group and Nitronic Ester: In acidity promoting action the nitro-group is about equivalent to two sulfones or three carbethoxy groups, i.e., the cfdx. are soluble in aqueous alkali.

A. Mode of action, questions involved:

1. Only empirical acidity or transformation into more acidic form

Evidence is as follows:

- Sulfonyl is purely acidifying - no enolization.
- Hantzsch obtain the nitronic acid, unstable.
- Nitro-ketones enolize and it is the carbonyl that is involved rather than the nitro-groups.

2. Constitution of acidic form:

- Old form of Hantzsch, $RCH \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} O \\ O \end{smallmatrix} N-OH$, cyclic.
- Present structure of " , $RCH::N \begin{smallmatrix} \cdot\cdot \\ \cdot\cdot \\ \cdot\cdot \\ \cdot\cdot \end{smallmatrix} \begin{smallmatrix} O \\ O \\ O \\ O \end{smallmatrix}$, does not explain active nitro compounds.

B. Nitro-compounds studied:

1. p-Bromophenylnitromethane, forms a nitronic ester with CH_2N_2 very rapidly in the aci-, slowly in normal-form. Ester decomposes by heating (80°) to p-bromobenzaloxime and $HCHO$.

2. Ethyl nitroacetate and methyl nitromalonate which do not enolize appreciably react vigorously to form nitronic esters with CH_2N_2 . Apparently a case of indirect methylation or addition to the $\cdot\cdot N=O$ ^{double bond} group in the nitro group.

3. p-Toluenesulfonylnitromethane: reacts with CH_2N_2 to form only nitronic ester.

4. o-Nitroacetophenone: $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} OCH_3 \\ C=CHNO_2 \end{smallmatrix}$ and $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} C \equiv CH=N-OCH_3 \end{smallmatrix}$ formed

Subject: The use of per-acetic acid as an oxidizing agent for organic compounds.

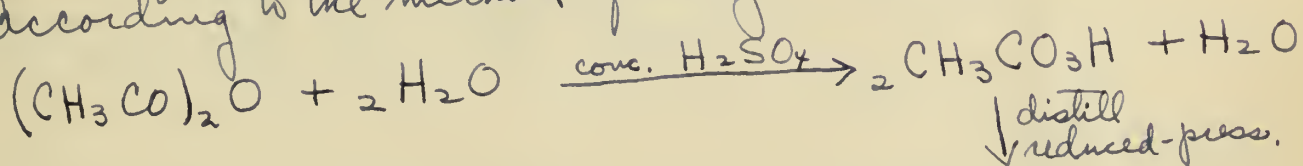
J. Böeseken and co-workers.

Best article: Oxidation of some phenols by per-acetic acid. A passage from the aromatic to the aliphatic series.
J. Böeseken and C.F. Metz, Rec. trav. chim. 54, 345 (1935).
(Org. Chem. Lab. of the Haute Ecole Technique, Delft, Holland)

Review article: Böeseken, Chem. Weekblad, 31, 166-70 (1934).

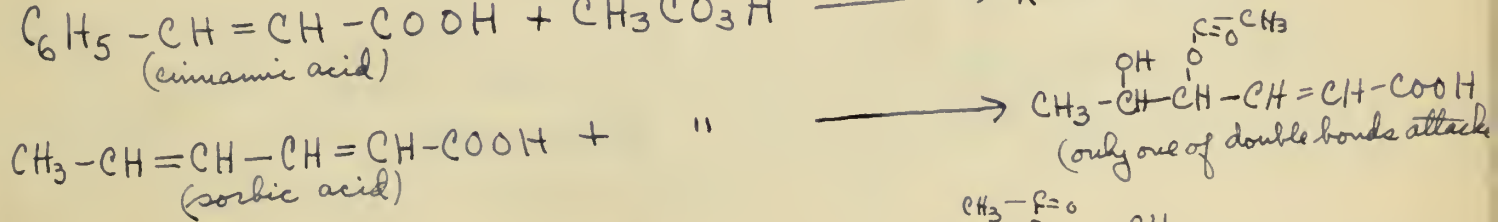
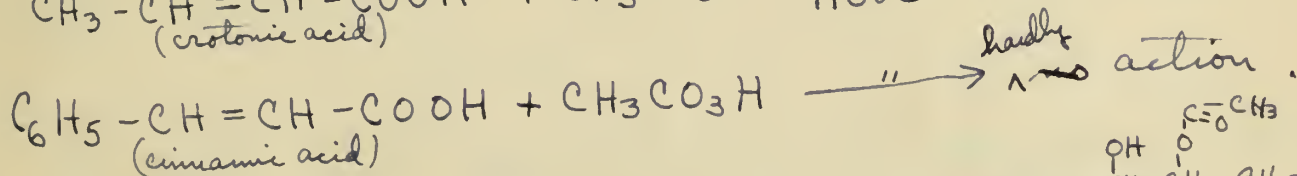
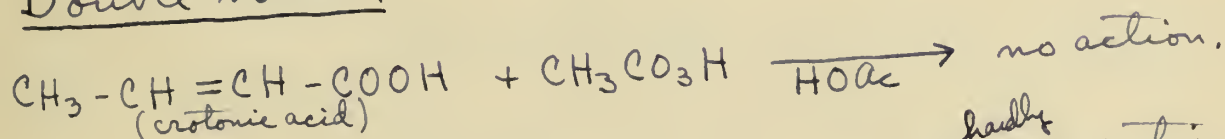
2. Preparation of per-acetic acid.

According to the method of Frey, Ber. 45, 1845 (1912).



3. Action of per-acetic acid on;

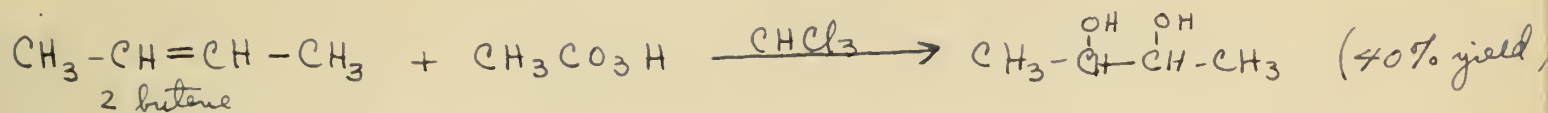
1. Double bonds:



The authors were unable to generalize as to the effect of the carbonyl or carboxyl upon the character of the >C=C< , except that

when the $C=O$ group was next to the $>C=C<$ the double bond was indifferent to the oxidizing action of per-acetic acid. (1)

39



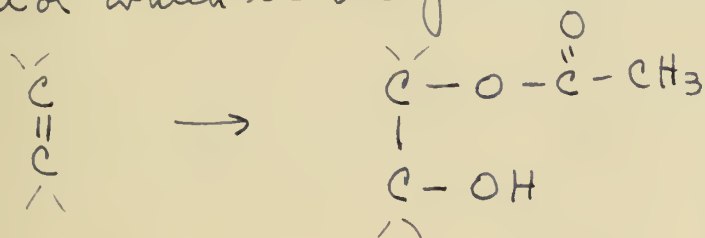
The two latter reactions show that if ~~the~~ the double bond is conjugated with a benzene nucleus, oxidation takes place rapidly - if the benzene nucleus is farther removed, oxidation is slower. (2.)

In general oxidation depends upon:

1. The number of H atoms attached to the unsaturated atoms
2. The character of the other groups.

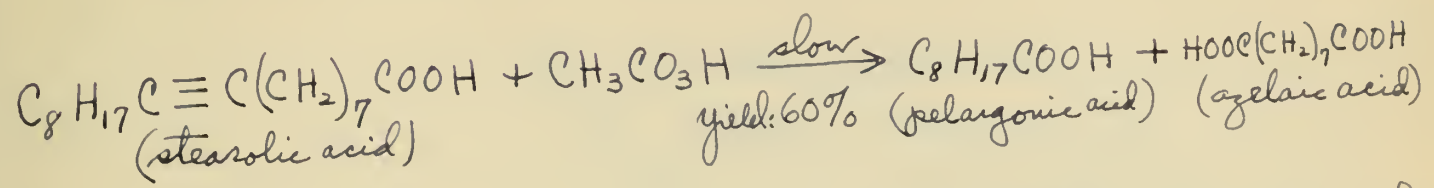
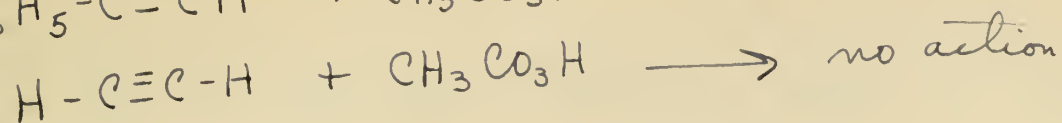
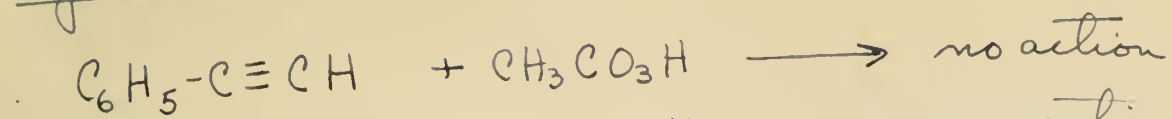
Mechanism:

The first step in the oxidation process is probably the addition of the reagent to the double bond, yielding the mono-acetate of a diol which is the product isolated in most cases.

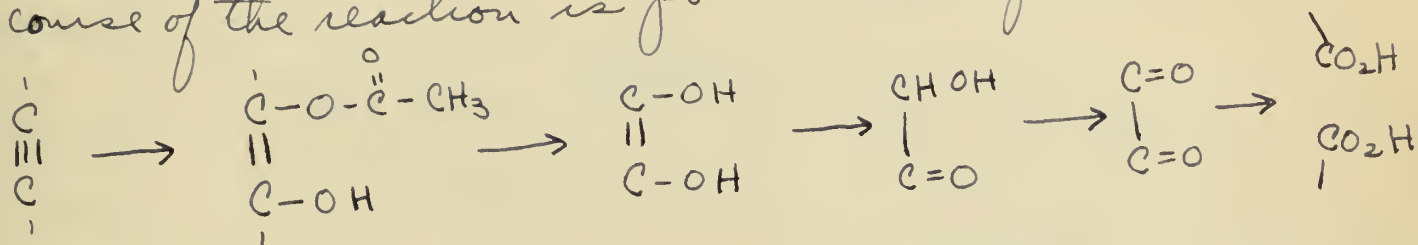


In a few cases (Me 9,12 linoleate) the ~~di~~ oxido derivative was isolated. ($=C^O=C^O=$) The isolation of this product was more frequent in the case of per-benzoic acid (2.).

- J. Böeseken, Rec. trav. chim. 45, 838 (1926).
 J. Böeseken & Maas Geesteranus, Rec. trav. chim. 51, 551 (1932).
 J. Böeseken & Elsen, Rec. trav. chim. 48, 363 (1929).
 J. Böeseken, Rec. trav. chim. 48, 322 (1929).

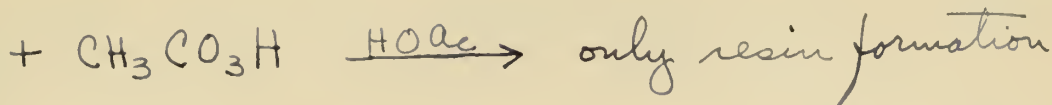
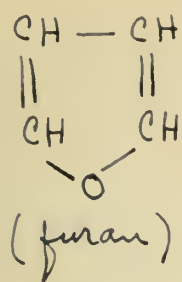
2. Triple-bonds:

Peracetic acid reacts very slowly with triple bonds. The course of the reaction is postulated as follows: (1)

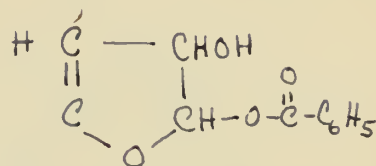
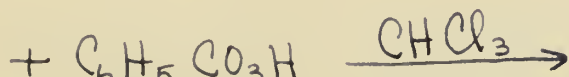
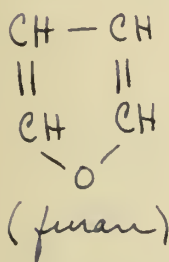


(1) Böeseken and Slooff, Rec. trav. chim. 49, 95-9 (1930).

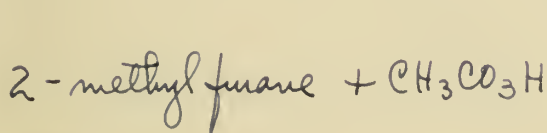
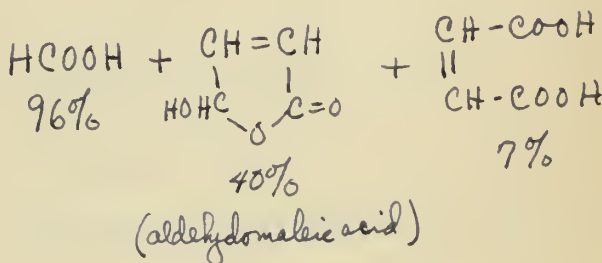
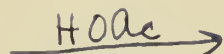
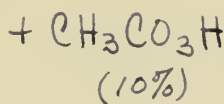
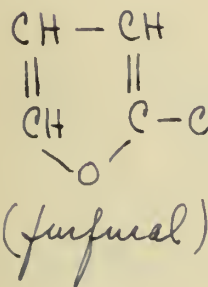
3. Furan and furan derivatives: (1).



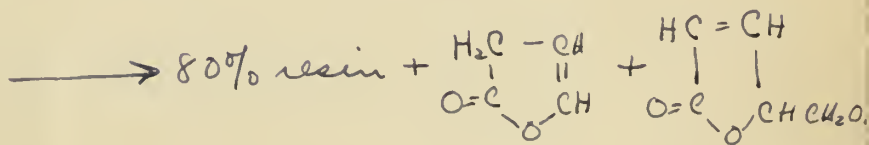
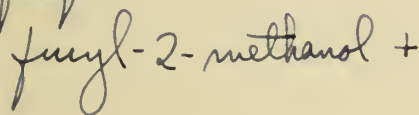
Note: The authors explain this behavior by postulating the initial formation of an oxide is $\begin{array}{c} \text{CH} - \text{CH} \\ || \quad || \\ \text{CH} \quad \text{CH} \\ \diagdown \quad \diagup \\ \text{O} \end{array}$ which in the presence of the acid (HOAc) tends to polymerize. This might find substantiation in the following reaction.



2-mono benzoate of 2,3 dihydroxy-2,3 dihydro-furan.

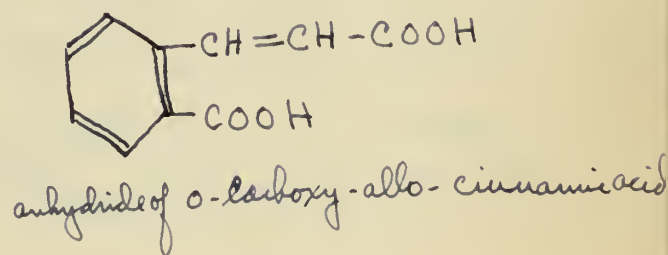
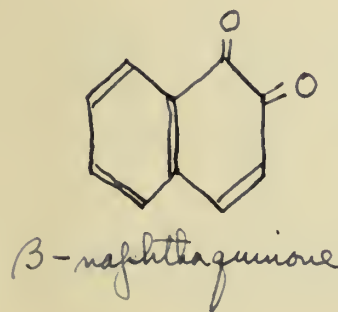
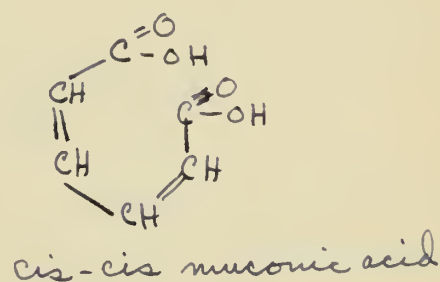
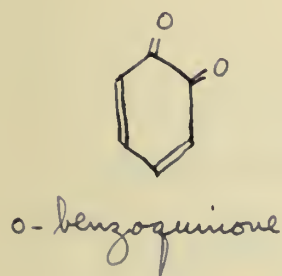
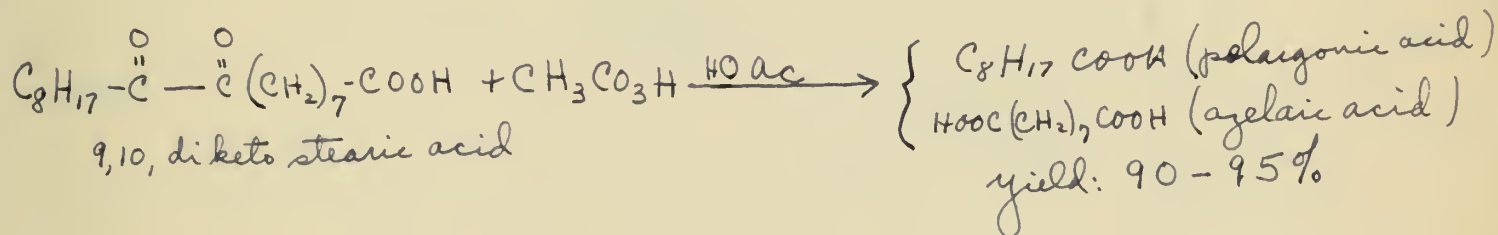
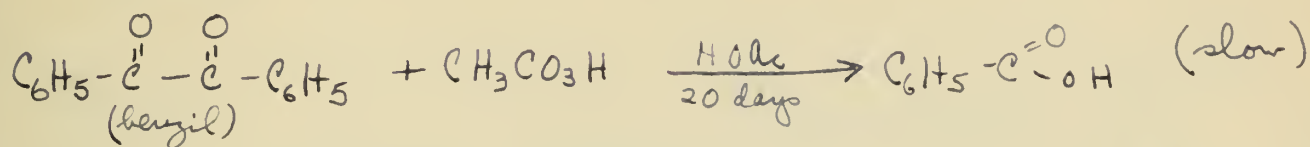
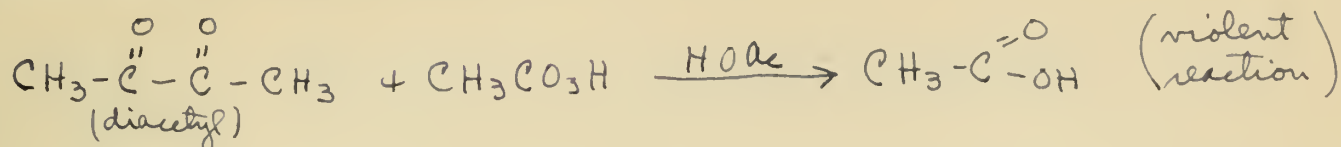


~~furyl~~

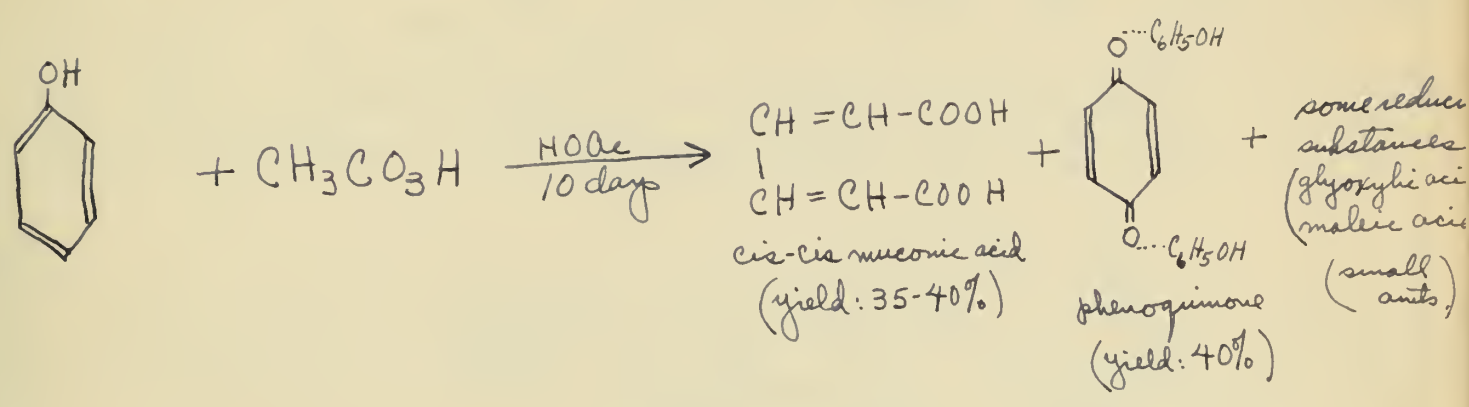


4. 1,2 di-ketones : (1)

42



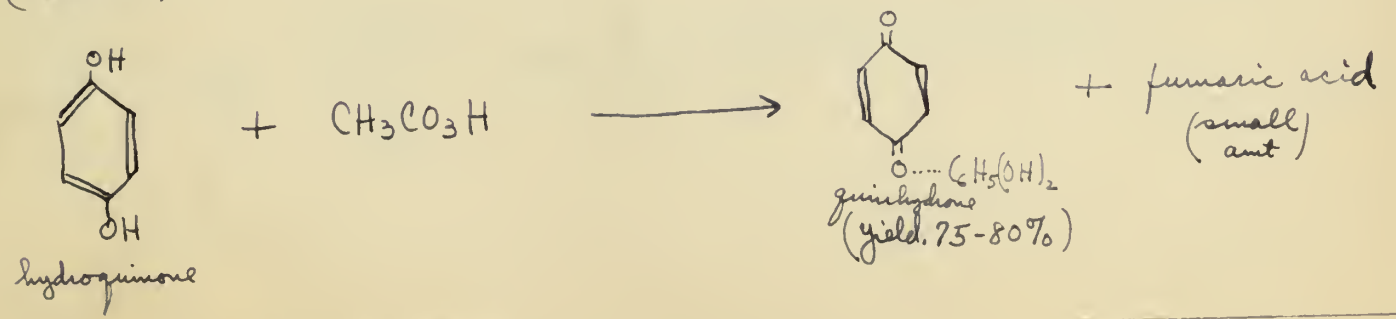
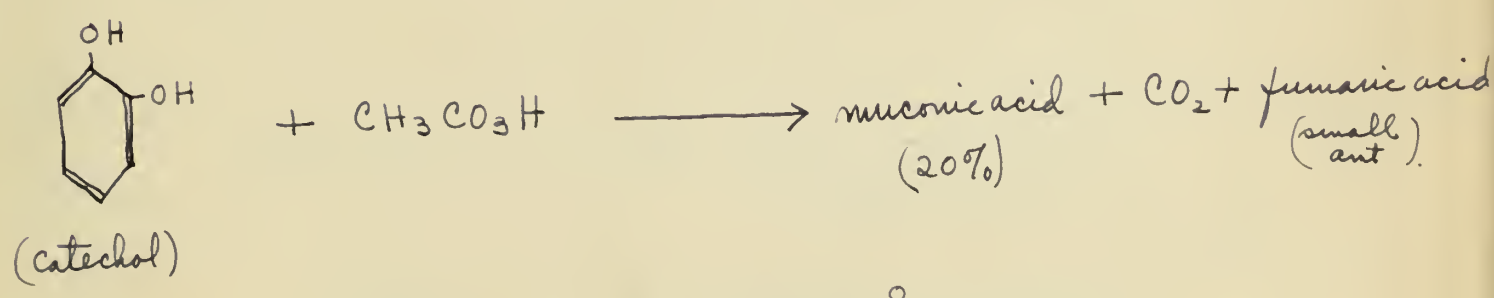
5. Phenols and substituted phenols:



In order to explain the formation of these two products, the authors postulate the following course of the reaction: (1.)

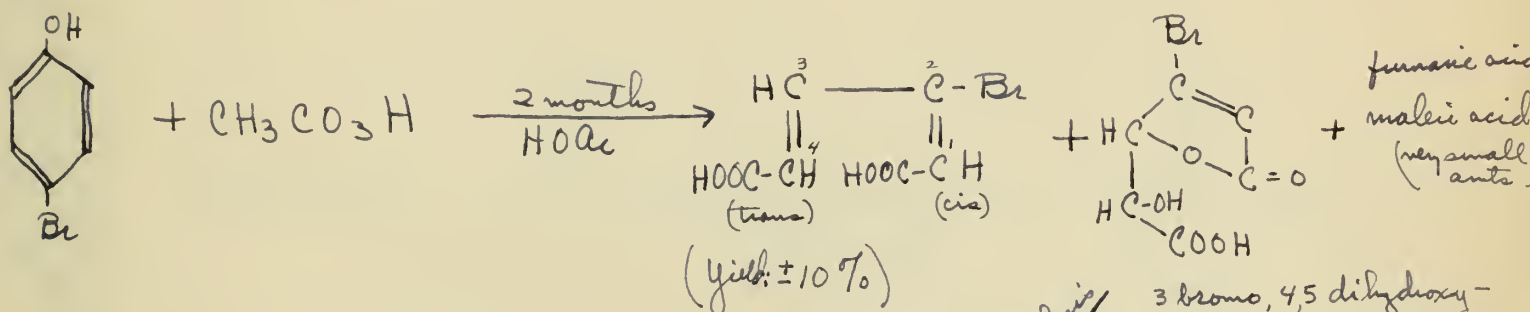
1. If the C-atom ortho to the -OH is attacked \longrightarrow o-quinone \longrightarrow muconic acid
2. If the C-atom para to the -OH is attacked \longrightarrow p-quinone $\xrightarrow{-\text{OH}}$ phenoguinone

Note: The above reaction constitutes a good synthesis for muconic acid. The authors have also found that the cis-cis muconic acid, when allowed to come in contact with free Br_2 or I_2 , changes over quantitatively to the stable trans-trans isomer (2.)

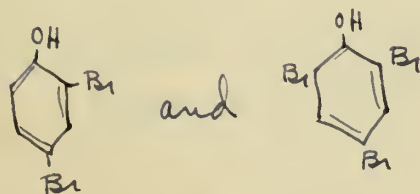
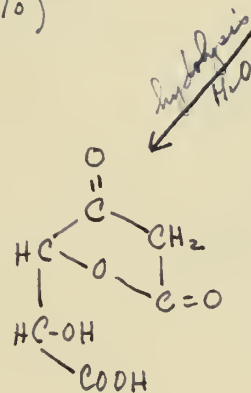


(1.) Böeseken, Proc. Acad. Sci. Amsterdam 35, 750-5 (1932); C.A. 27, 1333 (1933).
 (2.) Böeseken, Proc. Acad. Sci. Amsterdam 35, 750-5 (1932); C.A. 27, 1333 (1933).

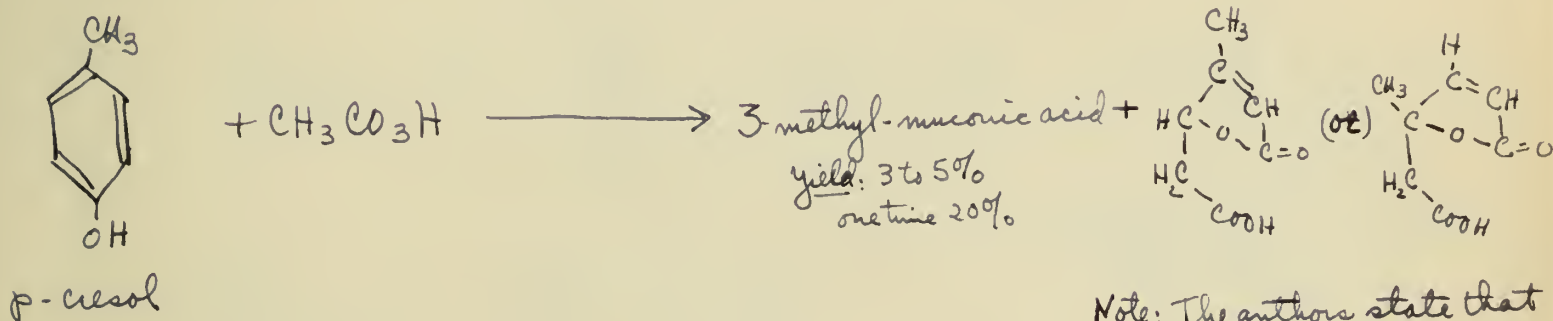
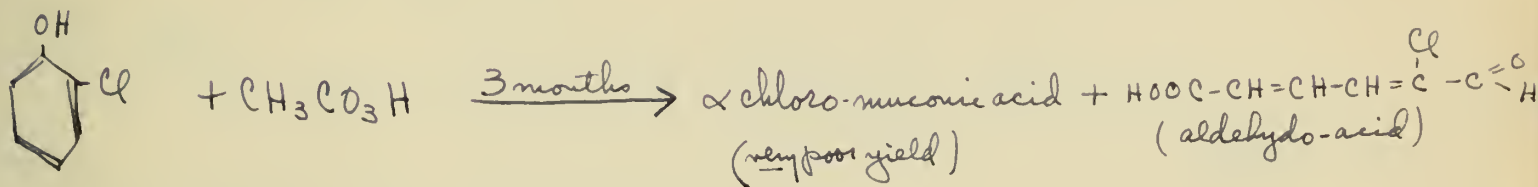
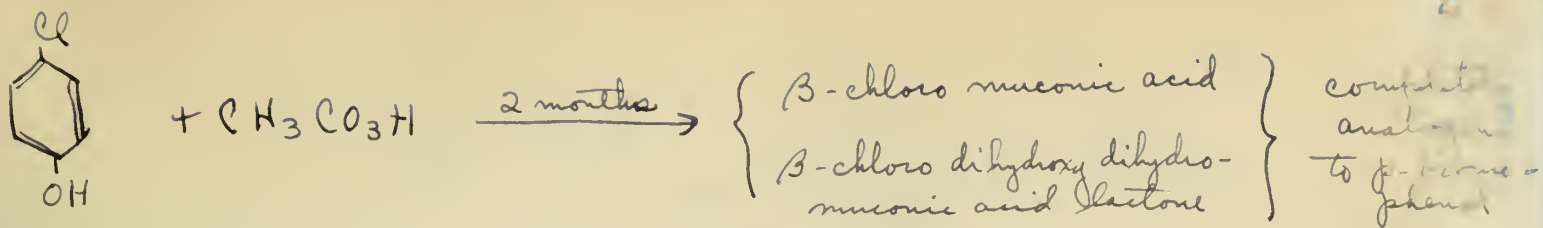
In consideration of the course of the reaction in the case of phenol, the authors reasoned that by substituting the *p*-position, the oxidation in the direction of *p*-quinone would be prevented, thereby forming exclusively and with increased yields, β -substituted muconic acids. It was found however that the oxidation proceeded more slowly and that the yields were poorer, accompanied by by products (lactones and hydroxy-lactones of β -subst. muconic acids).



Note: During this oxidation a little tri-bromo phenol is formed, which owes its existence to the formation of some free Br_2 . As was stated before this catalyst is able to stable the muconic acids. Since the β -bromo muconic acid isolated was stable the authors assign 1,2 double bond the cis config. (Br -repels COOH) and assign the 3,4 double bond the trans config. (1)



were not attacked by $\text{CH}_3\text{CO}_3\text{H}$.



Note: The authors state that a cyclization similar to the above occurs in the case of o-carboxy-cinnamic acid when heated above its melting point.

Summary:

Per-acetic acid is a useful oxidizing agent for organic compounds.

- 1.) Double bonds are converted to the mono-acetate of a diol
- 2.) Triple bonds are cleaved, yielding acids
- 3.) 1,2 diketones are cleaved, yielding acids
- 4.) Furan derivatives lead to a variety of products.
- 5.) In phenols and substituted phenols, oxidation occurs on the C-atoms ortho or (and) para to the phenolic hydroxyl in most cases, yielding the corresponding muconic acids.
- 6.) A good synthesis for muconic acid is found in the reaction between phenol and per-acetic acid.

The Occurrence of Free Radicals in Chem. Reaction

Heinrich Wieland & others

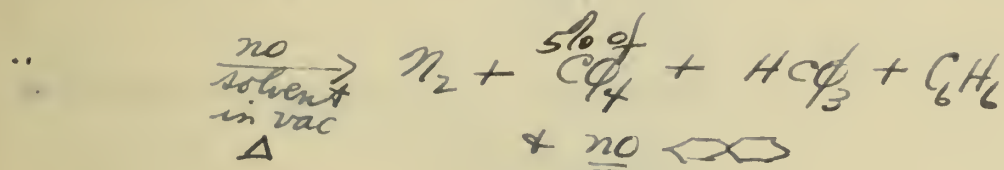
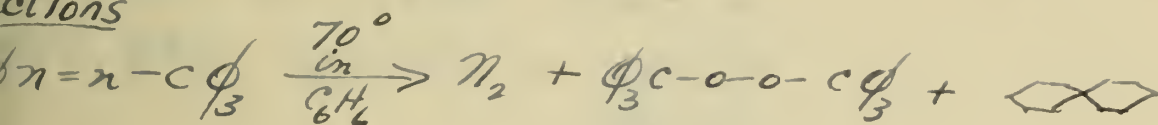
München

Ann 514-145 (1934)

work Bile Acids, Strychnos Alkaloids, Oxidation processes
Toad poisons.

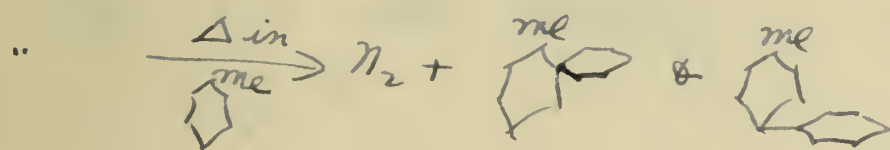
pose To study free radicals by thermal decomp. of azo compounds

ctions Deductions

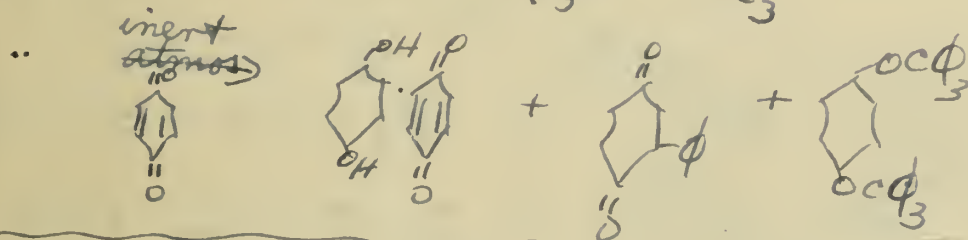
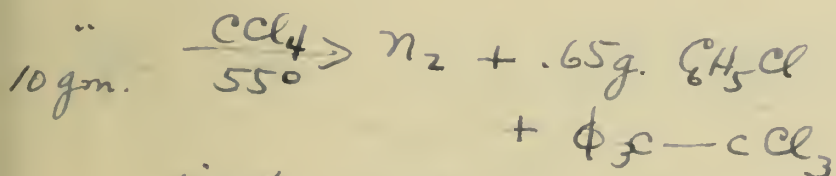


a) extra H must come from reac. mixture

b) phenyl radical does not unit with another C_6H_5



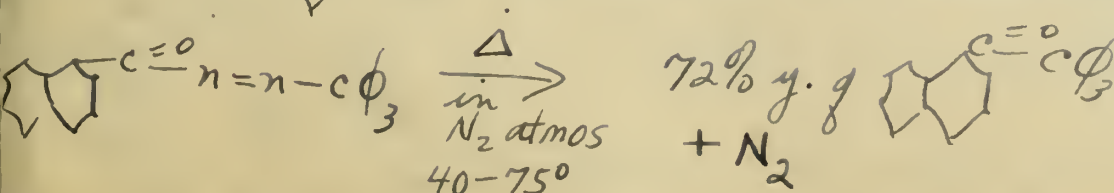
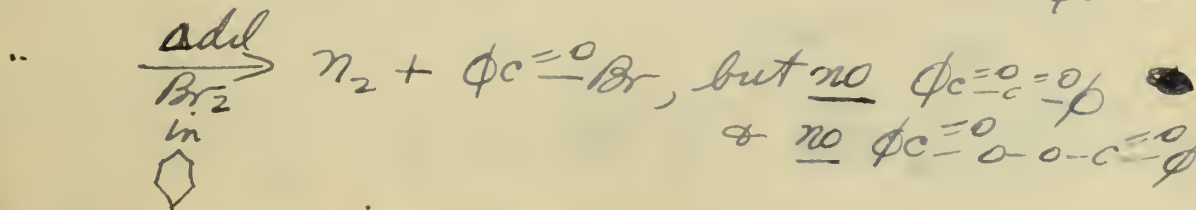
shows part played by solvent.



H in quinhydrone comes from reactn mixture.

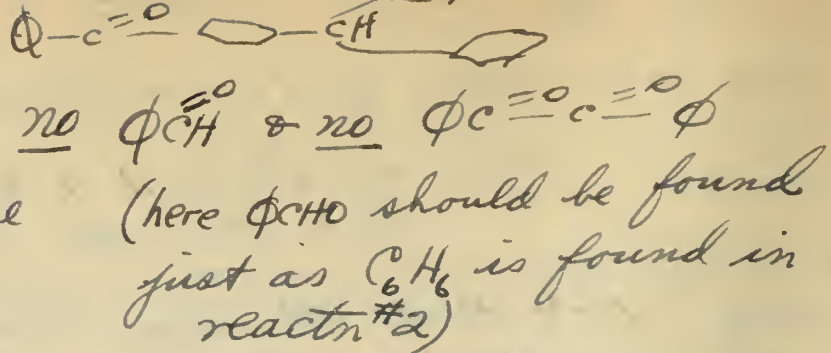
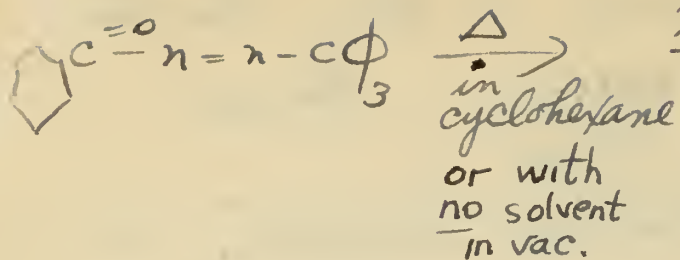


dem. reactivity of $\text{Ph-C}\equiv\text{O}$ radical



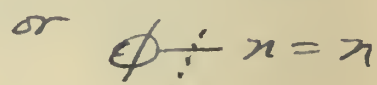
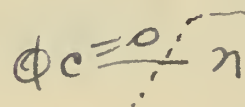
shows mech. of pyrolysis is different from that for reaction #2

(only 5% C_6H_6 in)

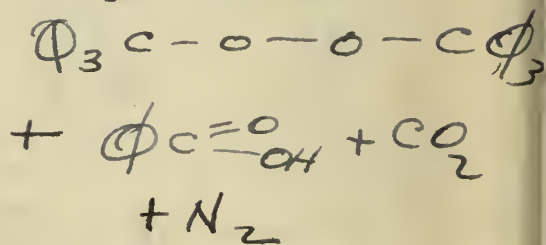
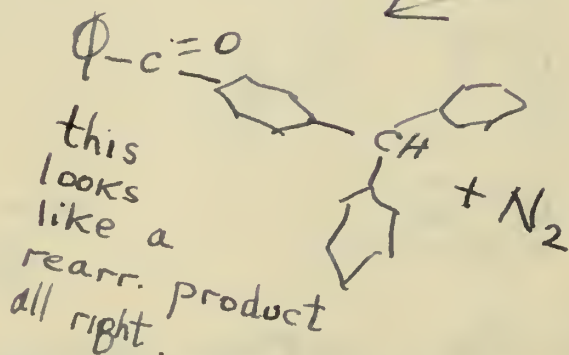
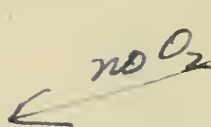
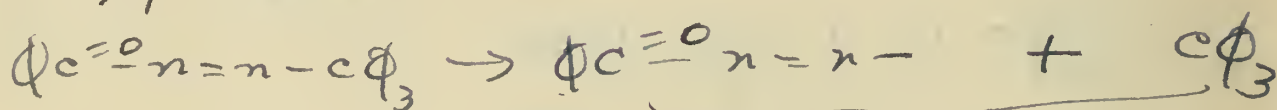


\therefore Wieland states mech. of pyrolysis of acyl azo compds. involves a rearr. within the molecule & then a decomp. with evol. of N_2

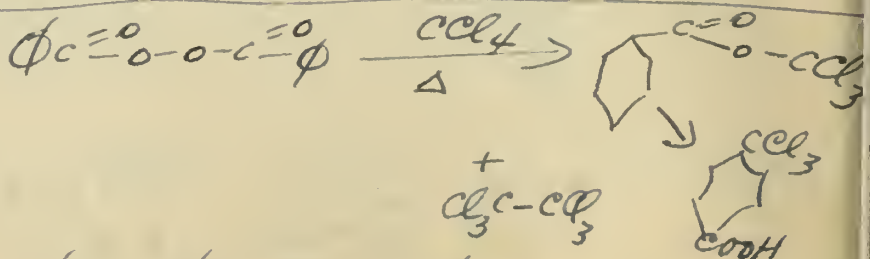
Further the bond is much more



\therefore reac. ^{might} proceed:



Previous work: Boeseken & Gelissen 1924

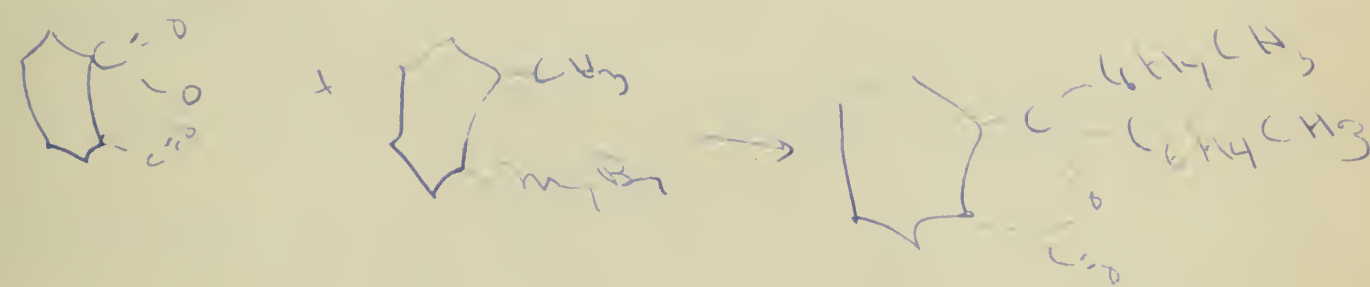


Note got very intense carmine red in decomp. products of the above azo compds, which decolorizes on shaking with O_2 or air. Analysis of these red solns. show spectrum bands not be

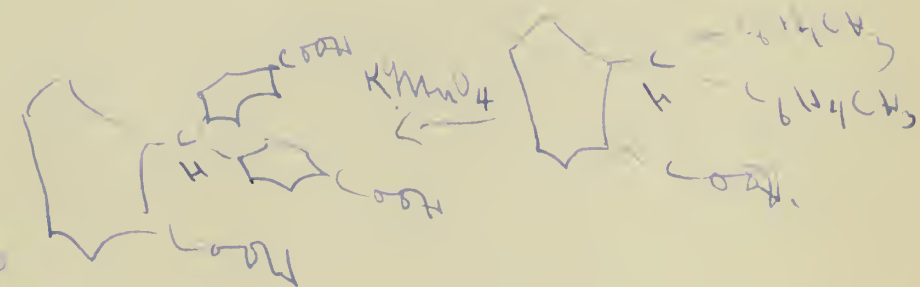
Triphenyl methane, whose benzene
 nuclei are connected to one another
 & Weiss Vinob.

Monat 65 124 1134

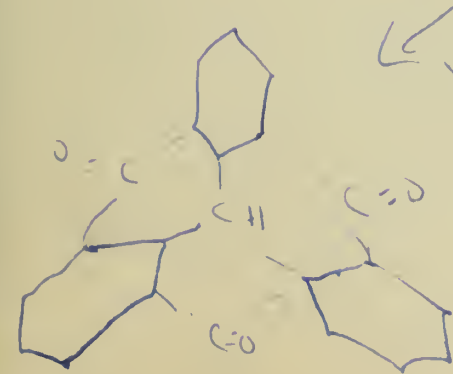
Preparation
 Fieser method



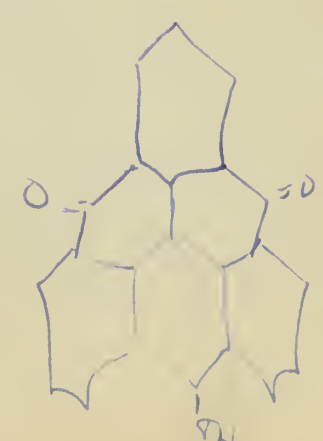
$\xrightarrow{H_2 (Hg)}$



$\xrightarrow{H_2SO_4}$



dehydration



This is used by dermal

Same series / compounds prepared from meso-phenyl chloride and p-xylene by the Friedel-Crafts reaction. & their ring closure by the above methods.

The compounds obtained were high melting ~~crystalline~~ solids which could not be easily obtained in a crystalline form due to their insolubility in all solvents.

Dr. Shriver does not believe the proof of structure is sufficient.

SUMMARY OF SEMINAR REPORT

by

Fred Condo

(April 24, 1935)

Topic: The Structure of Hydroxy-Azo Compounds

References: Richard Kuhn and Fritz Bär, Ann., 516,143 (1935)

(Heidelberg -- Carotenes, flavines, and
conjugated double bonds.)

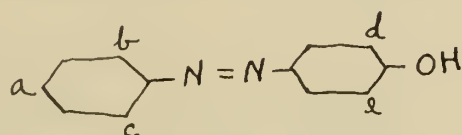
Lauer and Miller, J. Am. Chem. Soc., 57,525 (1935).

(U. of Minnesota -- α,β , Unsaturated ethers
and Miscellaneous.)

The fact that there are two general methods for the preparation of hydroxy-azo compounds, (a) the coupling of diazo compounds with phenols and (b) the reaction of substituted hydrazines with quinones, serves to immediately emphasize the question of the structure of these compounds. Reaction (a) would normally be expected to lead to an azo compound, while (b) should yield a hydrazone, but the same product is obtained in both cases.

The subject has an extensive bibliography including the names of many investigators. In recent years the great champion of the hydroxy-azo form has been von Auwers (working at Marburg), while the equally ardent defender of the quinone-hydrazone form has been Burawoy (until recently at Leipzig, now at the U. of London).

Lauer and Miller sought to test for the hydrazone form by use of the Diels and Alder reaction, adding cyclopentadiene to the quinone portion of the molecule. They found that cyclopentadiene would add to ~~the~~ benzoquinone-2,4-dinitrophenylhydrazone (2,4-dinitrobenzeneazophenol). The structure of the product was proven by adding cyclopentadiene to benzoquinone and reacting this product with 2,4-dinitrophenylhydrazine. The bis-hydrazone was formed, however, and in order to complete the structure proof, it was necessary to react the addition product of benzoquinone-2,4-dinitrophenylhydrazone with 2,4-dinitrophenylhydrazine. The results with other hydroxyazo-compounds were as indicated in the following table:



Added Cyclopentadiene

	<u>a</u>	<u>b</u>	<u>c</u>	<u>d</u>	<u>e</u>
1.	NO ₂	NO ₂		CH ₃	
2.	NO ₂	NO ₂		Br	
3.	NO ₂	NO ₂			

Did Not Add Cyclopentadiene

1.	NO ₂	NO ₂		Br	Br
2.		NO ₂			
3.	Br	NO ₂			
4.	NO ₂				
5.	COOH	NO ₂			
6.	NO ₂	Br	Br		
7.		COOH			
8.	SO ₃ H				
9.				COOH	
10.	OH				
11.	O-Ethers, acetates, and benzoates				

Kuhn and Bär attacked the same problem but with quite a different tool. They studied the absorption spectra. They worked first with phenyl-azo- α -naphthol and were able to show that the equilibrium between the azo and the hydrazone forms of this compound is dependent almost entirely upon the solvent. The method depended upon a comparison of the spectra in different solvents with the spectra of the O- and N- methyl ethers. In pyridine the spectrum indicated only the azo form, while in glacial acetic acid and in nitrobenzene only the hydrazone form was indicated. In benzene there seemed to be about equal amounts of the two forms, and in alcohol, while the azo form seemed predominant, there was distinct evidence of the hydrazone form also.

Investigation of the isomeric ortho compounds, α -phenylazo- β -naphthol and β -phenylazo- α -naphthol, indicated that these compounds exist only in the hydrazone form (confirming work of Burawoy), regardless of the solvent. It was impossible to prepare the O- ether of the β -naphthol and very difficult in the case of the α -naphthol.

Investigation of o-, m-, and p-hydroxy-azobenzene revealed that the structure of these compounds was also independent of solvent. But in this case all three of the compounds existed in the azo form only. (This is a direct contradiction of recent work by Burawoy in the case of the ortho compound.)

Attempts to isolate the two desmotropes of phenyl-azo- α -naphthol failed.

It was concluded from these two papers that in the hydroxy-azo- compounds there is an equilibrium between a hydroxy-azo form and a quinone-hydrazone form. The proportion of these two forms present at equilibrium varies very widely and is usually dependent upon the substituents (structure of the molecule) but may depend almost entirely upon the solvent.

Concerning 1,1,2,2-Tetraphenylcyclopropane
H. Wittig and B. Obermann
Ber 67 2053 (1934).

This is the sixth paper of a series on ring closures, radical formation and valence tautomerism of unsaturated systems. In previous papers the senior author (Wittig) studied the tetraphenyl ortho xylylenes. It was prepared from dimethyl phthalate by heating with lithium phenyl. The resulting glycol was methylated and the methyl ether cleaved with sodium potassium alloy forming the dipotassium derivative. When this was heated with tetramethylethylene bromide it formed 9,9,10 triphenyl dihydroanthracene. In another paper he studied the formation of 9,10-tetraphenyl dihydrophenanthrene from diphenic ester as indicated in the above procedure.

In this particular paper 1,1,2,2-tetraphenylcyclopropane was prepared from 1,1-diphenyl-2-benzyloxyethyl alcohol, which was made by treating malonic ester with phenylmagnesium bromide. The keto-carbinol was then converted to the glycol by means of lithium phenyl. This was then

2-
methylated with methyl alcohol having a trace of hydrogen chloride. This dimethyl ether on cleavage with sodium and potassium alloy yielded the 1,1,3,3-tetraphenylcyclopropane on treatment with tetramethylethylene bromide. The substituted cyclopropane is unusually stable toward boiling acetic acid and a boiling solution of bromine in carbon tetrachloride.

The 1,1,4,4-tetraphenyl-1,4-dipotassium butane yielded only unsymmetrical diphenylethylene on treatment with tetramethylethylene bromide. The 1,1,5,5-tetraphenyl-1,5-dipotassium pentane, prepared from dimethylglutarate and lithium phenyl as previously described, formed a polymeric hydrocarbon which on treatment with sodium and potassium alloy followed by decomposition with alcohol yielded the substituted pentane.

From this work it is concluded that the substituted cyclopropane, formed from intermolecular saturation, does not have a weakened valence bond between the substituted carbon atoms. In the case of the butane and pentane derivatives the molecules lose two potassium atoms forming unsymmetrical diphenylethylene and a polymeric hydrocarbon respectively.

QUINOLINE DICYANIDE: A CONTRIBUTION TO THE STEREOCHEMISTRY OF TRIVALENT NITROGEN.

References:

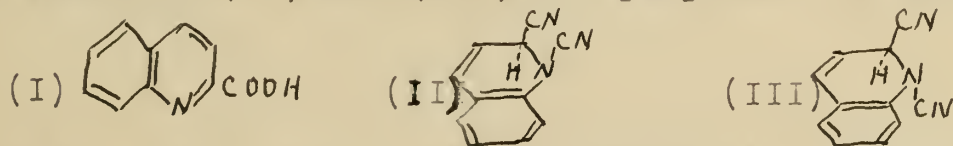
- O. Mumm and H. Ludwig, Ann. 514, 34-60 (1934).
 O. Mumm and Herrendorfer, Ber. 47, 758 (1914).
 O. Mumm and Bruhn, Ber. 68, 176-83 (1935).

Location of the authors:

Chemical Institute of the University of
Kiel, Germany.

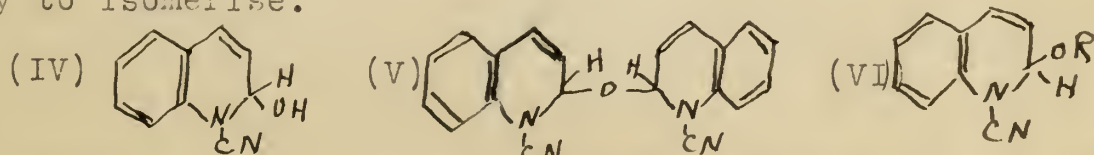
Quinoline when treated with ErCN and anhydrous HCN in dry benzene solution at 0° , yields a dicyanide, $\text{C}_9\text{H}_7\text{N}(\text{CN})_2$, which melts at 100° . Treatment of this compound with a basic nitrogen compound, such as ammonia or methylamine, converts it to an isomer melting at 130° . Reactions and properties indicate that these are stereoisomers; i.e., cis and trans forms.

Both isomeric dicyanides yield quinaldinic acid (I) on hydrolysis. Therefore formulas (II) and (III) are proposed for these isomers.



This is the first case in which evidence has been found favoring the existence of stereoisomers where a trivalent nitrogen is involved.

Quinoline and BrCN only, in dry benzene, reacts to yield N-cyano- α -hydroxy-dihydroquinoline (IV) and the bimolecular compound (V). This is probably due to the action of a trace of moisture on the BrCN addition product. Neither the hydroxy nor the alkoxy compounds (VI) show any tendency to isomerise.



Substituents in the o-position of the benzene ring or the α -position of the pyridine ring block the formation of dicyanides and only γ -cyanoquinolines are obtained from compounds whose rings are so substituted.

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SEMINAR TOPICS

I Semester 1935-36

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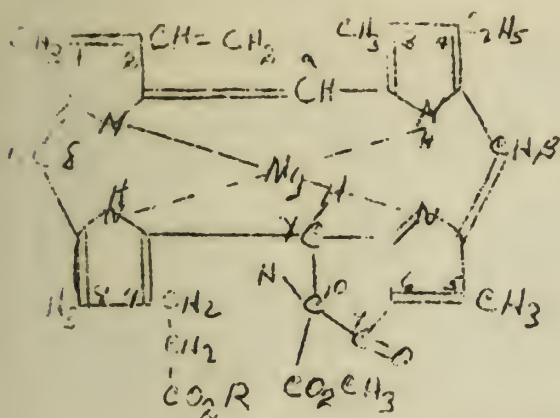
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Further Contributions on the Structure of Chlorophyll

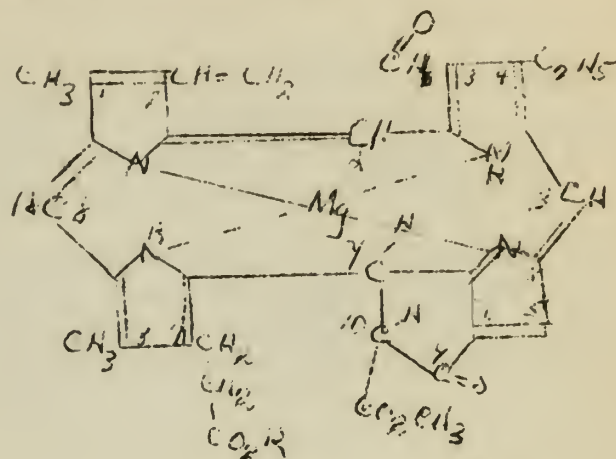
H. Fischer and co-workers at the
Technical High School at Munich. Ann. 513, 107
(1934); 516, 61 (1935); 519, 1, 58 (1935);

*Dietz, J. Chem. Ed., 12, 208 (1935);
Armstrong, Chem and Ind., 52, 809 (1935).*

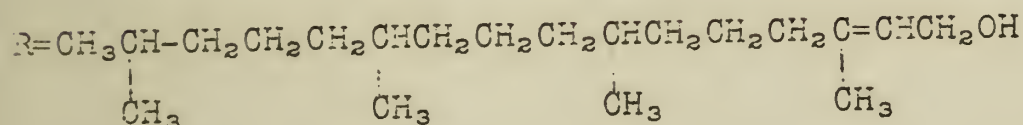
Introduction: Fischer's latest proposed formulae for chlorophyll-a and -b are:



Chlorophyll (a)
I



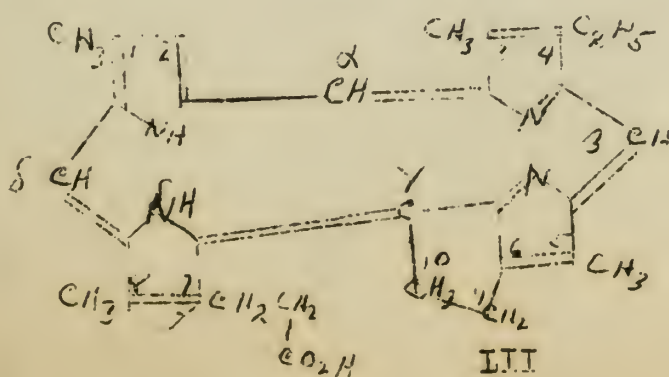
Chlorophyll (b)
II



These papers are concerned with

- I Proof of the presence of the vinyl group at the 2-position in chlorophyll-a.
- II Proof of the presence of the formyl group at the 3-position in chlorophyll-b.
- III The asymmetry of the gamma-carbon atom.

I After the magnesium atom and the phytyl radical are removed, the vinyl group is converted to an acetyl group by the action of hydrogen iodide in glacial acetic acid. This acetyl group, together with the carbomethoxy group on carbon atom 10 and the oxygen atom on carbon atom 9, is replaced by hydrogen upon treatment with hydrogen bromide in glacial acetic acid at 190° in a bomb. The new substance is 2-desethyl-desoxophylloerythrine (III). This compound was synthesized,

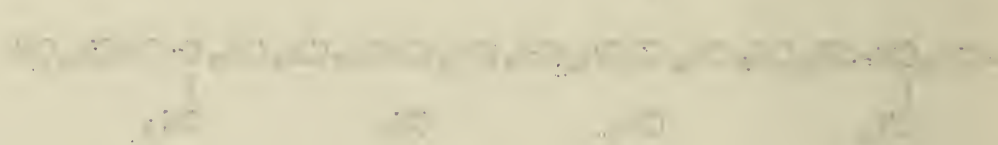
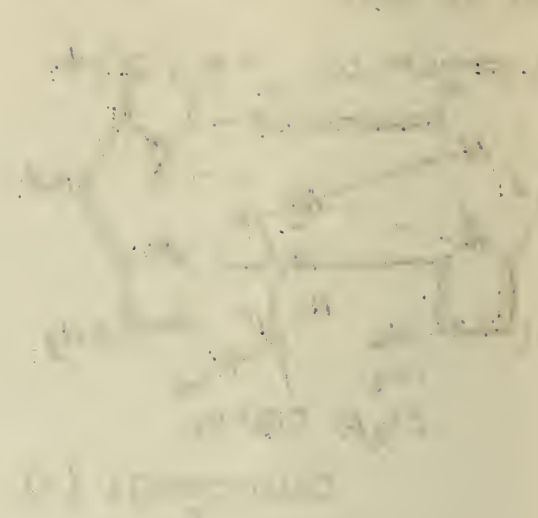
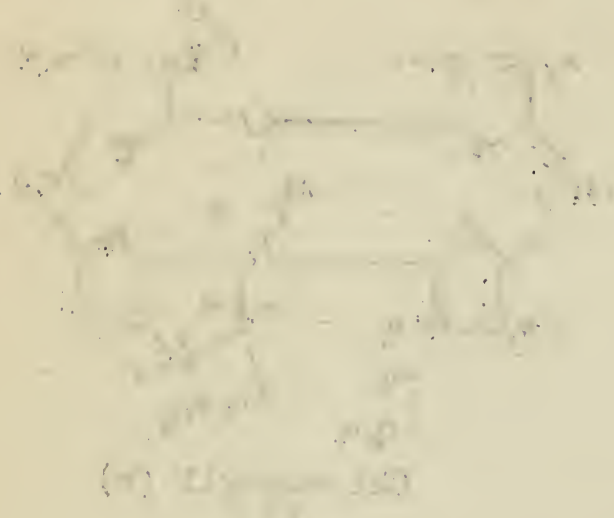


III

20 Jan 36 9. Roger Adams

Published by the American Medical Association, 535 North Dearborn Street, Chicago, Ill.
Subscription price, Five Dollars per Annum in Advance. Single Copies, Fifteen Cents.
Entered as Second-Class Matter, May 26, 1894. Postpaid at Special Rate of \$3.00 per Annum.
Acceptance for mailing at Special Rate of Postage provided for in Act of October 3, 1911.
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The Effect of the Diet on the Blood Pressure in the Human Being
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and the synthetic product shown to be identical with the one from chlorophyll-a.

II In a similar way 3-desmethyldesoxophylloerythrine was prepared and shown to be identical with the product obtained from chlorophyll-b by causing it to undergo the same reactions, save for that with hydrogen iodide, that chlorophyll-a was submitted to.

III Optical activity of chlorophyll derivatives was supposed to be due entirely to the asymmetry of carbon atom 10. Replacement of the carbomethoxy group with hydrogen yields a product still optically active. Asymmetry of the gamma-carbon atom is therefore postulated.

Reported by Dr. S. H. Babcock, Jr.
September 18, 1935

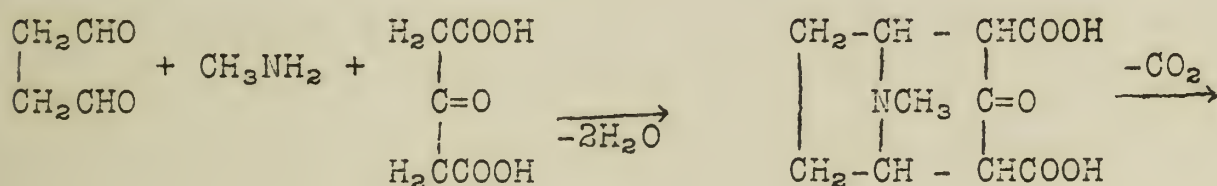
Synthesis of Tropinon, Pseudopelletierin, Sobelanin, and related alkaloids under physiological conditions.

Clemens Schöpf and Gerhard Lehmann
Ann. 518, 1 (1918).

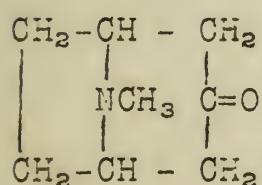
The authors report syntheses of tropanone and a number of other closely related alkaloids or intermediates. The starting materials and conditions in most cases are such as could exist in plant cells where these compounds are synthesized naturally. The point is stressed that natural products such as alkaloids, glucosides, etc. are probably synthesized in plants without the aid of catalysts such as enzymes and that attempts should be made to prepare such compounds in vitro under mild conditions. This investigation was suggested by a previous observation of the authors concerning the condensation of α amino benzaldehyde with β keto acids. If this reaction is carried out at pH 13 the product is an α substituted quinoline β carboxylic acid, but if the pH is from 5 to 9 the reaction goes smoothly, with good yields, to form α substituted quinolines. Here as in later attempts to synthesize alkaloids better yields are obtained nearer neutrality than in strongly acidic or alkaline solutions. Since the starting materials need no special purification, the reactions are easily run and the yields good, these methods may be suitable for synthesis of quantities of these products.

Tropanone (II) was prepared by allowing a mixture of succindialdehyde, methylamine, and acetone dicarboxylic acid to stand together at warm temperature for 3 days. Yields obtained from reaction mixtures having different pH are tabulated below and it will be noticed that yields are greater near the point of neutrality than at the extremes of pH.

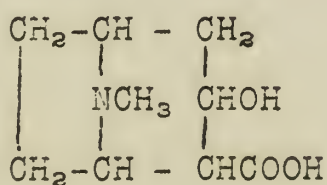
pH of reaction mixture	3.0	5.0	7.0	9.0	11.0	13.0
Percent of theoretical yield	68	83	78	61	64	5



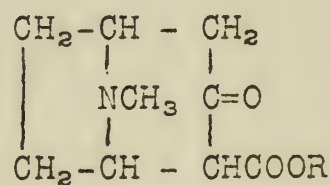
I



II



IV



V (R=H); VI (R=CH₃)

The authors disagree with the theory of Robinson that ecgonine (IV) is formed in the plant cell by elimination of one carboxyl group from tropanone dicarboxylic acid (I). They suggest that cocaine may be formed by condensation succindialdehyde, methyl amine, and the mono methyl ester of acetone dicarboxylic acid to form tropanone monocarboxylic acid methyl ester (VI) (which they prove by experiment) and a subsequent reduction of the carbonyl group

followed by benzylation.

Several other alkaloids and intermediates were also prepared. Glutaraldehyde, methyl amine and acetone dicarboxylic acid condense under proper conditions (with elimination of H_2O and CO_2) giving good yields of pseudopelletierin. If acetone is substituted for acetone dicarboxylic acid no reaction takes place. Sobelanin was prepared by condensation of glutaraldehyde, methyl amine, and benzoyl acetic acid. Two alkaloids not occurring naturally, N-methyl α, α' diphenacyl pyrrolidin and N-methyl α, α' diacetyl pyrrolidin, were prepared.

Reported by A. E. Knauf
September 18, 1935

The Stepwise Degradation and the Constitution of β -Carotene

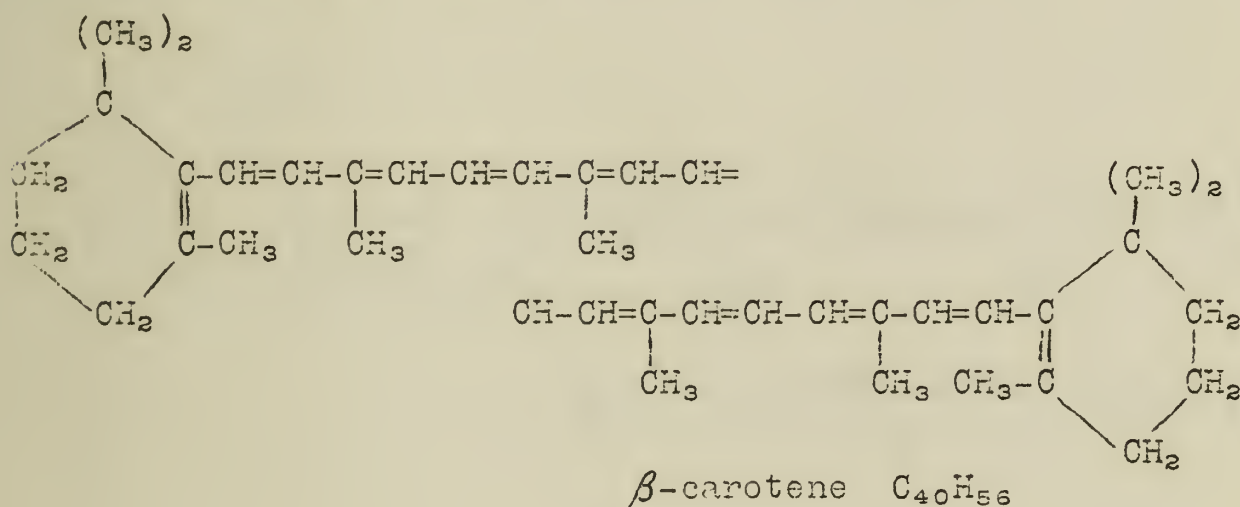
von Richard Kuhn and Hans Brockmann
Ann. 516, 95-143 (1935)

Place: Kaiser Wilhelm-Institute for Chem., Heidelberg

Previous Work: 1. Carotenes, carotenoids, anthocyanins, chlorophylls and flavins

2. Structure of Hydroxy-azo-compounds

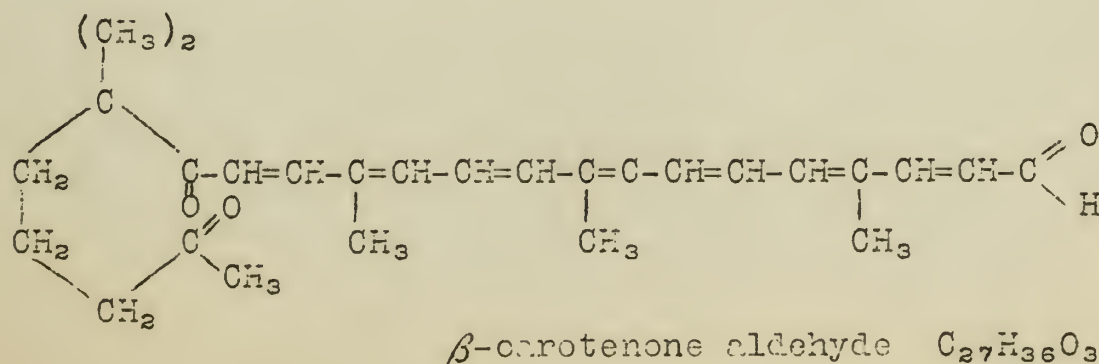
Only limiting proof has been obtained for the constitution of the pigments of the carotene-series with the exception of lycopin. The following work confirms the structure assigned by Karren (Helv., 13, 1084 (1930)) to β -carotene, who, by strong oxidation obtained geronic acid from β -carotene (16 percent of the theory for the two ionon rings).



In an earlier work Kuhn, (Ber., 67B, 885-888 (1934)), oxidized β -carotene with chromic acid and obtained an aldehyde which he converted to the amide via the oxime and nitrile. This amide was dehydro-azafrenone amide. No experimental work was given.

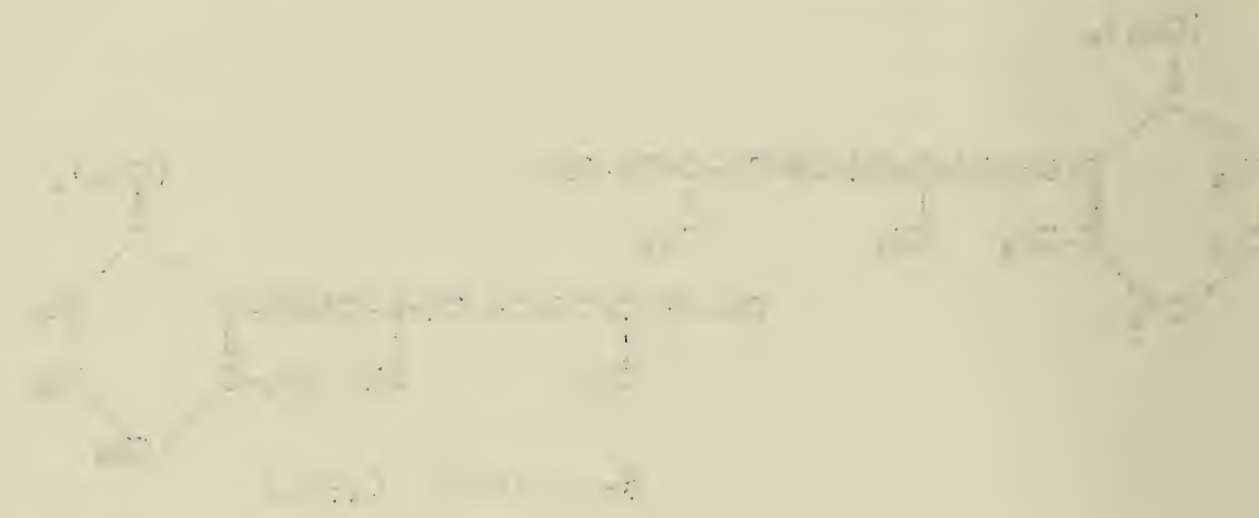
This work is a continuation of the first and definitely establishes the structure of β -carotene.

β -carotene was oxidized by the alternate use of chromic acid and a mixture of chromic acid and lead tetraacetate to β -carotene-aldehyde.



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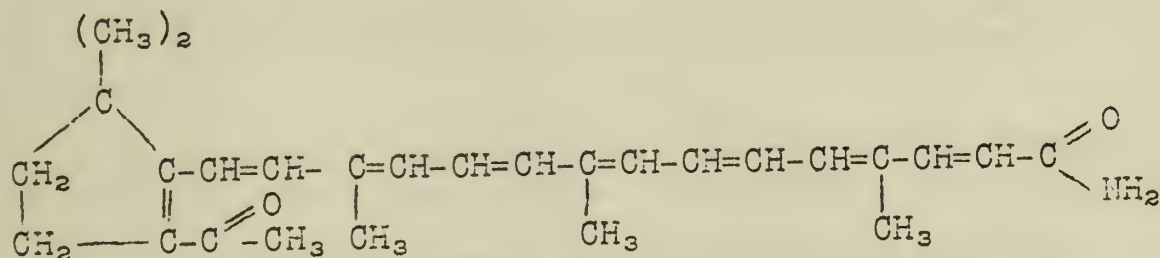
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β -carotenone-aldehyde was converted through the oxime and nitrile to anhydro-azafrenoneamide $C_{27}H_{37}O_3N$. Azafrene was then used as starting material for the synthesis of anhydro-azafrenoneamide showing clearly the relation between β -carotene and azafrene.

Kuhn establishes the position of the methyl groups by thermal decomposition of azafrene which gives m-tolylc acid and m-xylene.



Reported by R. F. Miller
September 25, 1935

The Constitution of Alkannin

Randnitz et al.,	Ber.	68,	1479	(1935)
"	"	67,	1955	(1933)
"	"	65B,	159	(1932)
"	"	64,	1835	(1931)

From the laboratory of the German University at Prague.

In 1930 Randnitz showed by color reactions and spectra that alkannin did not compare with known anthraquinone derivatives and products, even though it did give anthracene derivatives on zinc dust hydrogenation.

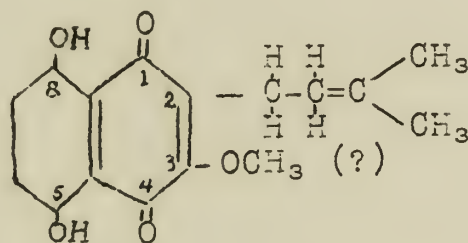
It did compare with a 5,8-tetrahydro-1,4-dihydroxy naphtha quinone derivative. He concluded that it belonged to the naphthalene C skeleton. It contained two hydroxyl groups and two quinone O atoms. It could be by reduction acetylated to a tetra acetyl-levo-alkannin.

By catalytic hydrogenation two ethylenic linkages in the side chain were shown. His analysis was $C_{16}H_{14}O_4$.

He repeated his work and confirmed it in 1931.

In 1932 he showed that a compound $C_{17}H_{18}O_5$ (alkannin plus one MeO group picked up from the methyl alcohol used in purification) took up 7 mols of H with Pt.

It yielded with ozone 0.7 mol of acetone and by reduction with Zn and NaOAc in boiling Ac_2O a tetra-acetyl dihydro alkannin. The product he concluded to be,



In 1935 Randnitz obtained the dyestuff in pure form without the methylation and his analysis was $C_{16}H_{16}O_5$. He made the methyl ether and coupled it with 2,3-dimethyl butadiene and showed that the side chain was on the hydroquinone and not on the quinone nucleus; also, that the CH_3O group was on the side chain and not on the nucleus as previously supposed.

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FROM THE UNIVERSITY OF CHICAGO
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The University of Chicago Library is pleased to announce the acquisition of a new volume, *The University of Chicago Library*, published by the University of Chicago Press. This volume is a comprehensive guide to the library's collections and services, and is available in both print and electronic formats.

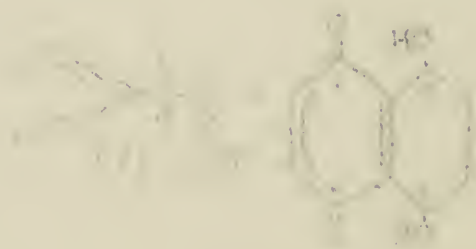
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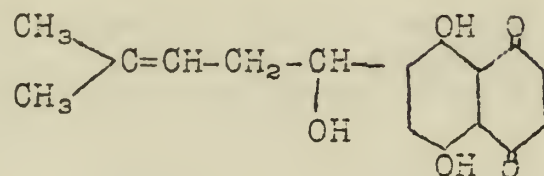
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Diazomethane also added on the nucleus confirming the positions so the new formula for alkannin is as follows:



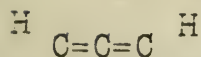
Brand (Ber. 68, 1488) obtained angelic acid from the red oil which later gave the crystalline product so that alkannin is the ester of angelic acid.

Reported by R. C. Cary
October 2, 1935

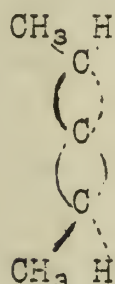
RESOLUTION OF ALLENIC COMPOUNDS

By E. P. Kohler, J. T. Walker
and H. Tishler. J. Amer. Chem. Soc.
57, 1743-45 (1935), Harvard University

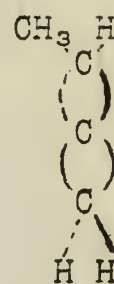
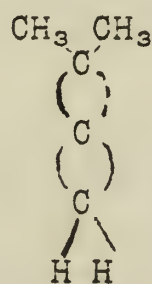
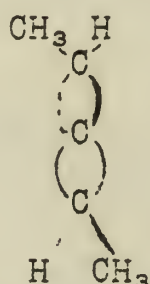
In the simplest cumulative double bond compound



H, it is necessary only to replace one hydrogen at each end to obtain non-superposable mirror images using the tetrahedral model of the carbon atom as proposed by van't Hoff in 1877.



d,l forms of sym.
dimethyl allene



Non-resolvable
unsymmetrical dimethyl
allene.

For 50 years, efforts to confirm the optically active character of properly substituted allenes as predicted by van't Hoff have met with failure.

Recently Ziegler and Sauermilch have prepared a number of allenes by dehydration of unsaturated tertiary alcohols. Using Ziegler's general method for preparing allenes, Mills and Maitland claim to have succeeded in verifying van't Hoff's prediction of enantiomorphism in unsymmetrically substituted allenes.

Mills used a process of catalytic asymmetric degra-

$$\begin{array}{c} \text{C}_6\text{H}_5 \\ \diagdown \\ \text{C}=\text{C}-\text{C}-\text{OH} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{C}_6\text{H}_5 \\ \text{C}_{10}\text{H}_7 \end{array}$$
 dation on C_{10}H_7 . With no catalyst an inactive allene, m.p. 244° , was obtained. With d-camphor sulfonic acid, an isomeride, m.p. 159° , having a rotation of $[\alpha]_{546} + 437$ was produced. With l-camphor sulfonic acid the rotation was -433 . The two antipodes were readily obtained pure but when mixed and crystallized from solution the racemic form, m.p. 244° , was recovered. The active forms lose their activity slowly at 160°C .

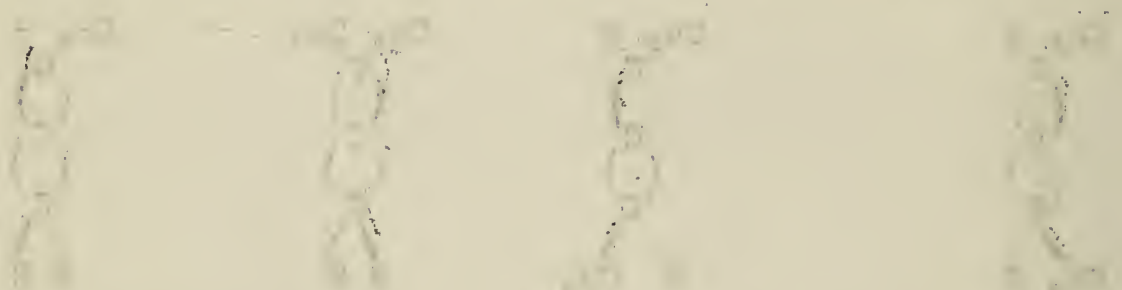
Some time prior to the publication of Mill, the announcement of the preparation of the first authentic allenic acid was made from the Illinois laboratories and it was predicted that certain types of allenic acids would prove to be easily synthesized.

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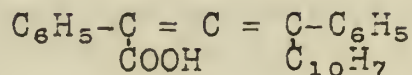
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-2-

Kohler, who has worked in this field for many years, decided that the compound



prepared and characterized by Lapworth and Wechsler in 1910 was really an allene and not an indene which Lapworth and Wechsler thought it might be. The synthesis involved treatment of diphenyl naphthyl butyrolactone with PCl_5 . HCl was evolved and upon treatment with pyridine and $\text{C}_2\text{H}_5\text{OH}$ the ester $\text{C}_6\text{H}_5-\underset{\text{COOC}_2\text{H}_5}{\text{C}} = \text{C} \begin{array}{l} \text{---} \text{C}_{10}\text{H}_7 \\ \text{---} \text{C}_6\text{H}_5 \end{array}$ was formed.

This was converted to the acid chloride which on reaction with glycollic acid gave $\text{C}_6\text{H}_5-\text{C}=\text{C}=\underset{\text{C-O-CH}_2\text{-COOH}}{\overset{\text{O}}{\text{C}}}-\text{C}_6\text{H}_5$

The brucine salt of this derivative was crystallized from methyl alcohol. On treatment with HCl , the pure acid, m.p. 145° was precipitated. The rotation was $+29.5$. A mixture of the d and l forms, m.p. 145° , gives on crystallization the racemic acid, m.p. 195° , which is identical with that obtained by hydrolysis of the ethyl ester. The structure of these was proved by oxidation to phenyl naphthyl ketone and phenyl glyoxylic acid.

Reported by W. J. Sparks
October 2, 1935

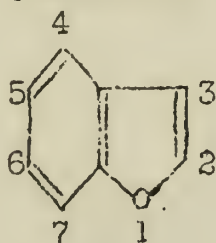
SYNTHESIS OF COUMARONE-2-CARBOXYLIC ACID AND HYDROXYCOUMARONES

By: T. Reichstein, R. Oppenaur,
A. Grusser, R. Hirt, L. Rhyner and
G. Glatthaar. *Helv. Chim. Acta.*
18, 816 (1935).

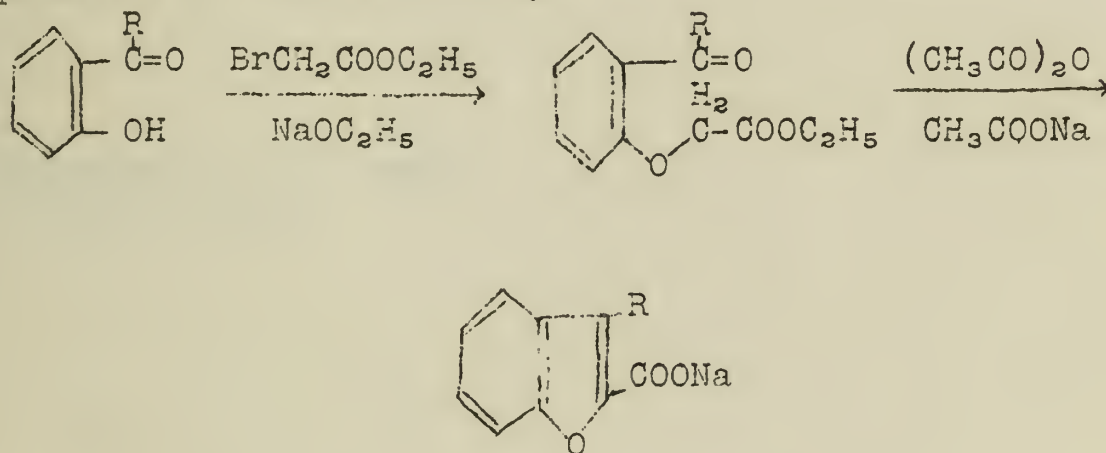
Place: Organic Chemistry Laboratory of the
Eidg. Techn. High School, Zurich.

Previous work: Methylfurans, 2-Isopropyl-
furan, Isotubaic acid.

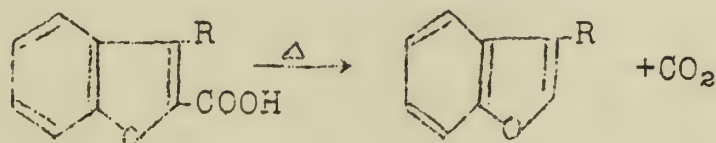
Coumarone



Reichstein and co-workers have shown that a slight modification of Rossing's (*Ber.* 17, 3000 (1884)) synthesis has proved successful in the preparation of many of the substituted coumarones which have been impossible to obtain before.



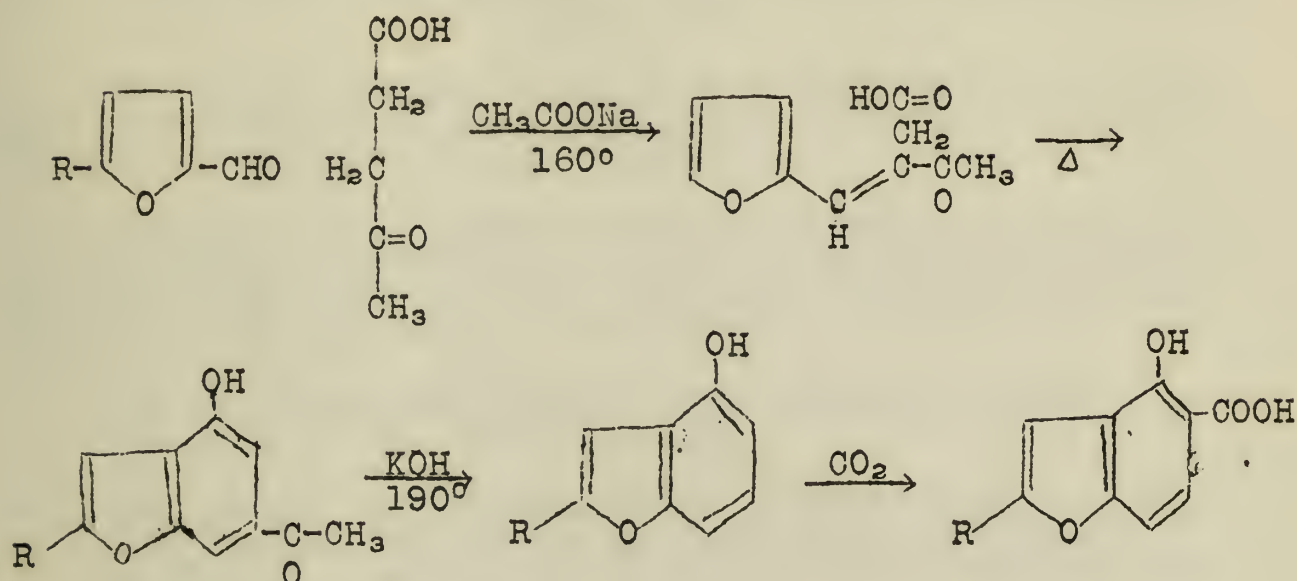
Removal of the carboxyl group is accomplished by treating the acid with copper-bronze powder in a boiling solution of quinoline.



The various substituted coumarones that were made by this method were prepared by replacing the salicylaldehyde by the following compounds, o-vanillin, pyrogallol, 2-hydroxy-3, 4-dimethoxybenzaldehyde, resorcyal-aldehyde-4-benzyl ether, phloroglucinaldehyde-2-methyl-4-benzyl

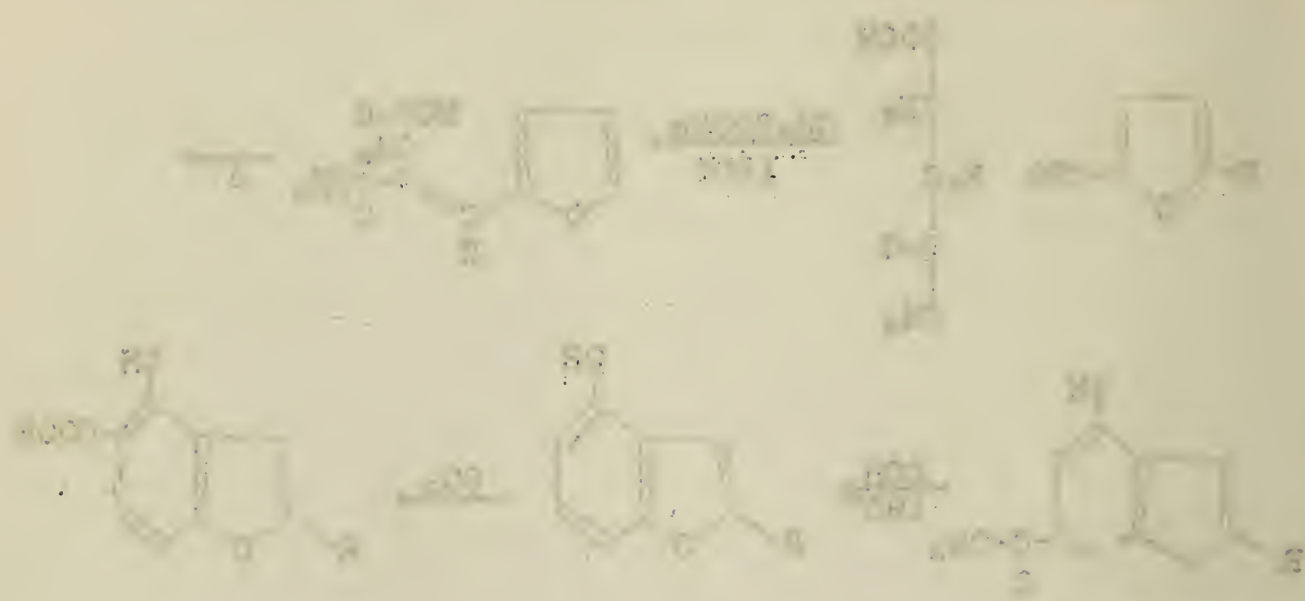
ether and 2,4-dihydroxyisobutyrophenone.

An alternate method has had a limited application.



Reported by L. R. Drake
October 9, 1935

Journal of Polymer Science, Part A: Polymer Chemistry
 Vol. 10, 1001-1010 (1972)



Received May 15, 1972
 Revised July 10, 1972

BF₃ forms molecular complexes with certain types of organic compounds. A considerable number of these complexes have been isolated and characterized ^{1,2,3,4}, and they are in general monomolecular addition compounds of BF₃ and the organic compound.

e.g. CH₃OH·BF₃, CH₃CO₂H·BF₃, (C₂H₅)₂O·BF₃, (CH₃CO)₂O·BF₃,
C₆H₅NH₂·BF₃

The BF₃ is thought to be held to the organic molecule by a coordinate-covalent linkage with the O or N atom as "donor" and the B atom as "acceptor".

Although these complexes have been known for some time, their practical importance has been recognized only within the last 5-10 years and they have been utilized with some success in various organic reactions.

- (1) Alcohols and glycols with acetylene in the presence of BF₃ yield acetals⁵.
- (2) Acids and alcohols react in the presence of BF₃ to give fair yields of the corresponding esters⁶. Similarly, acetates may be formed from acetamide and alcohols in the presence of BF₃⁷.
- (3) Alkyl aryl ethers are rearranged by BF₃ to phenols, alkyl phenols, and alkyl phenyl ethers⁸.
- (4) Propylene may be condensed with phenols in the presence of BF₃ to yield isopropyl aryl ethers, isopropyl phenols, and the isopropyl ethers of these isopropyl phenols⁹.
- (5) Propylene may be condensed with acids in the presence of BF₃ to yield isopropyl esters¹⁰, and in the case of hydroxybenzoic acids, these are rearranged to give isopropyl hydroxybenzoic acids and their esters¹¹.
- (6) Ethers are cleaved by acid chlorides and acid anhydrides in the presence of BF₃ to yield esters¹².
- (7) BF₃ may be substituted for AlCl₃ in reactions e.g. the synthesis of ketones and β-diketones¹³.
- (8) Phenols are alkylated by alcohols to the corresponding ethers with BF₃¹⁴.
- (9) Propylene and other olefins condense with aromatic hydrocarbons to give the alkyl hydrocarbons in the presence of BF₃¹⁵.
- (10) Certain alifatic hydrocarbons, both open-chain and cyclic, have been condensed with ethylene in the presence of BF₃ to yield higher hydrocarbons¹⁶.

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1. Nieuwland, et al, J. Am. Chem. Soc. 53, 3909 (1931)
2. Meerwein, et al, Chem. Abstracts 26, 1371; J. prakt. Chem. 141, 123 (1934)
3. Morgan and Taylor, Chem and Ind. 50, 869 (1931); J. Chem. Soc. 1932, 1497.
4. O'Leary and Wenzke, J. Am. Chem. Soc. 55, 2117 (1933)
5. Nieuwland, et al, J. Am. Chem. Soc. 52, 1018 (1930)
Proc. Indiana Acad. Sci. 40, 203 (1931)
6. ibid., 54, 2017 (1932)
7. ibid., 55, 5052 (1933)
8. ibid., 54, 2019 (1933); 55, 3402 (1933)
9. ibid., 54, 3694 (1932)
10. ibid., 56, 2689 (1934)
11. ibid., 56, 2054 (1934); 57, 1549 (1935)
12. ibid., 55, 2857 (1933)
Meerwein, et al, J. prakt. Chem. 134, 51 (1932)
13. Meerwein, et al, Ber. 66B, 411 (1931); J. prakt. Chem. 141, 149 (1934)
14. Nieuwland, et al, J. Am. Chem. Soc. 57, 709 (1935)
15. ibid., 57, 1547 (1935)
16. Ipatieff, et al, J. Am. Chem. Soc. 57, 1616, 1722 (1935)

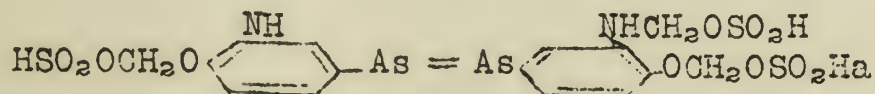
Reported by M. F. Roy
October 9, 1935

CONSTITUTION OF SULPHARSPHENAMINE

By: Dyke and King, J. Chem. Soc.,
1933, 1003; J. Chem. Soc., 1934, 805.

Place: National Institute for Medical Research.

The structure of sulpharsphenamine had been given by the authors to be the sodium salt of 3,3'-diamino-4,4'-dihydroxy-arsenobenzene-0,0',N-trimethylene sulfite.



This formulation was built on the following experimental considerations:

1. Proof of presence of three methylene sulfite groups as a part of the molecular structure.
2. Only one of the three groups was oxidized to sulfate by alkaline iodine.
3. Authors had shown that mono-N-methylene sulfites of anilines gave a quantitative yield of sulfate by the same treatment.

Mainly from these facts, the authors concluded that of the three groups the one capable of undergoing oxidation by the alkaline iodine conditions was an amine derivative while the other two were on the phenolic hydroxyls. The main objections to the formula were the difference in reaction indicated by the O- and N-methylene sulfite groups toward alkaline iodine, and the fact that no methylene sulfites of phenolic hydroxyls had been prepared.

In the present work the authors submit evidence toward a new formula.

1. Formation of a tetramethylene sulfite derivative of salvarsan from which less than one mol of sulfate be precipitated by the iodine method. This showed that an O-union of the group was not necessary for prevention of oxidation.
2. Preparation of *o*-aminophenol derivative with an excess of sodium bisulfite and formaldehyde to yield a dimethylene sulfite which formed a trisodium salt, and in which only a portion of the sulfite could be oxidized to sulfate by iodine.
3. In reaction of anilines with performed sodium formaldehyde sulfite, a mono-N-methylene sulfite was formed, which gave a quantitative precipitation of sulfate by iodine.
4. Erratic results in sulfate quantities on oxidation and difference in mono-N- and N,N-dimethylene sulfite toward oxidation by the same reagent indicated an intermediate sulfur form. Authors have considered a dithionate formation.

CONSTITUTION OF THE UNITED STATES

BY THE PRESIDENT OF THE UNITED STATES
JAMES MONROE, 1800-1817

Printed by the National Institute for Historical Research
Washington, D.C.

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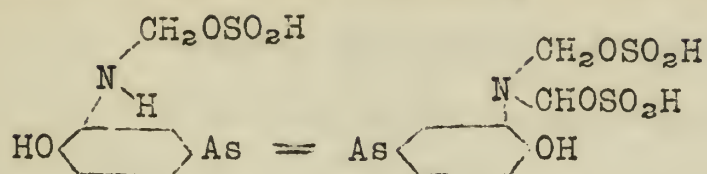
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2. Second of the series of the Constitution of the United States, as published by the National Institute for Historical Research.
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In the present work, the authors of the various editions of the Constitution of the United States have been able to compile a list of the names of the authors of the various editions of the Constitution of the United States, as published by the National Institute for Historical Research.

1. Formation of a special committee to study the Constitution of the United States, as published by the National Institute for Historical Research.
2. Formation of a special committee to study the Constitution of the United States, as published by the National Institute for Historical Research.
3. Formation of a special committee to study the Constitution of the United States, as published by the National Institute for Historical Research.
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9. Formation of a special committee to study the Constitution of the United States, as published by the National Institute for Historical Research.
10. Formation of a special committee to study the Constitution of the United States, as published by the National Institute for Historical Research.

From these results the authors present the new formula



for sulpharsphenamine, and suggest a series of new compounds of interest.

Reported by L. L. Alexander
October 16, 1935

From these results the authors conclude that the reaction



for nitrobenzene, as shown in the reaction scheme, is

Reported by C. J. Aldrich
October 11, 1955

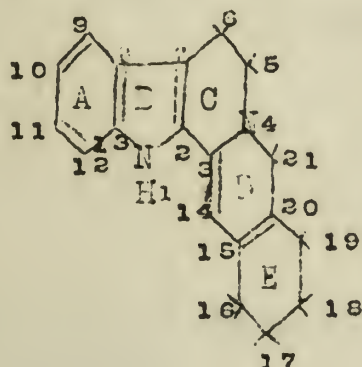
ON THE CONSTITUTION OF YOHIMBINE

By: Caesar Scholz.
 Helv. Chim. Acta., 18,
 923 (1935).

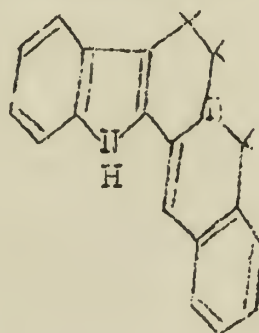
Place: University of Edinburgh.

Previous work: Alkaloids (Harman).

Yohimbine ($C_{21}H_{26}O_3N_2$) yields upon selenium dehydrogenation yobyryne, tetrahydroyobyryne and ketoyobyryne. The present paper is concerned with the structure of the degradation products.



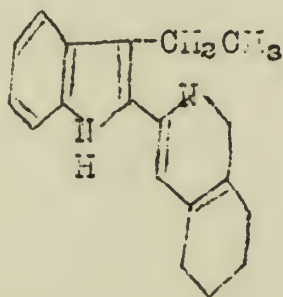
Tetrahydroyobyryne
 $C_{19}H_{20}N_2$



Yobyryne
 $C_{19}H_{16}N_2$

The above formulae were those accepted for these compounds before the present work.

Tetrahydroyobyryne yields upon ozonization a compound $C_{19}H_{20}O_2N_2$. The same compound is obtained on treatment with chromic acid. Hydrolysis of this compound yields *o*-aminopropiophenone and Bz-tetrahydroisoquinoline-3-monocarboxylic acid. Oxidation leads to berberonic acid. In view of the above, tetrahydroyobyryne is



Yobyryne gives no clear-cut ozonization product, but oxidation leads to oxy-yobyryne $C_{19}H_{14}ON_2$.

On purely circumstantial evidence, the secondary hydroxyl group present in yohimbine is placed in the 14 position, and

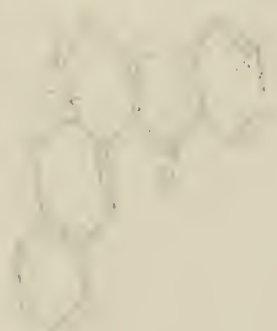
ON THE TOXICITY OF TETRAHYDROXYMETHYL

BY
J. H. HARRIS, JR.
AND
J. H. HARRIS, JR.

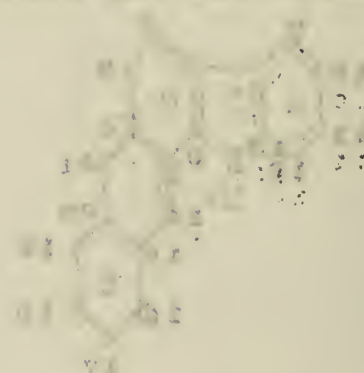
From the University of California

Received April 15, 1934

Tetrahydroxymethyl is a highly toxic substance which has been found to be highly toxic to a wide variety of animals. It is a colorless, odorless, and tasteless liquid which is miscible with water. It is a powerful irritant to the skin and mucous membranes, and it is also a powerful emetic and cathartic. It is a highly toxic substance which has been found to be highly toxic to a wide variety of animals.



Tetrahydroxymethyl



Tetrahydroxymethyl

The above formulae are those assigned for these compounds before the present work.

Tetrahydroxymethyl is a highly toxic substance which has been found to be highly toxic to a wide variety of animals. It is a colorless, odorless, and tasteless liquid which is miscible with water. It is a powerful irritant to the skin and mucous membranes, and it is also a powerful emetic and cathartic. It is a highly toxic substance which has been found to be highly toxic to a wide variety of animals.

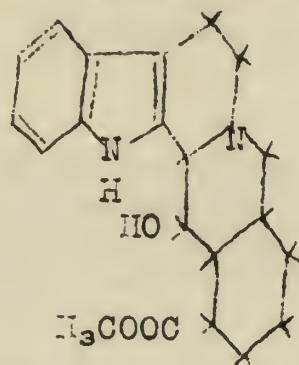


Tetrahydroxymethyl is a highly toxic substance which has been found to be highly toxic to a wide variety of animals. It is a colorless, odorless, and tasteless liquid which is miscible with water. It is a powerful irritant to the skin and mucous membranes, and it is also a powerful emetic and cathartic. It is a highly toxic substance which has been found to be highly toxic to a wide variety of animals.

On account of its high toxicity, tetrahydroxymethyl is a highly toxic substance which has been found to be highly toxic to a wide variety of animals. It is a colorless, odorless, and tasteless liquid which is miscible with water. It is a powerful irritant to the skin and mucous membranes, and it is also a powerful emetic and cathartic. It is a highly toxic substance which has been found to be highly toxic to a wide variety of animals.

-2-

the structural formula is believed by Scholz to be



Reported by H. G. Kolloff
October 16, 1935

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The structure formula is given by means of



Reported by R. G. Kellie
October 10, 1933

Michel Lesbre

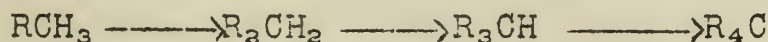
Bull. Soc. Chim., (5) 2, 1189 (1935)

Lab. of Gen. Chem., Sorbonne.

Kozeschkow, K. A., Ber., 66, 1661, (1933)

The A and B subdivisions of the fourth group in the periodic table differ widely in their tendency to form organic compounds. Those under silicon form organic compounds more or less comparable, in their formation and properties, to carbon compounds.

The following series of compounds are arranged in order of decreasing stability:



The Sn-H bond is much less stable than the C-H bond. Sn-Sn bonds are rare.

A nomenclature, analogous to that of carbon compounds, is suggested:

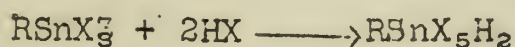
$\text{Sn}_n\text{H}_{2n} + 2$	RSnOOH	R_3SnOH	R_2SnO
Stannanes	Stannonic acids	Stannols	Stannones

The methods of producing stannonic acids and stannones are analogous to those for the production of aliphatic acids and ketones.

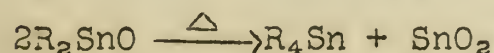
The reactions of SnO_2KH with CH_3I and of HCl_2K with CH_3I show a fundamental difference in the structure of stannites and formates. The potassium atom must be attached directly to the tin atom.

The reaction of KSnO_2 with halogen derivatives has been made general for the production of stannonic acids.

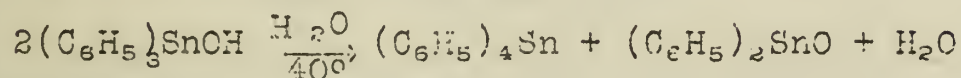
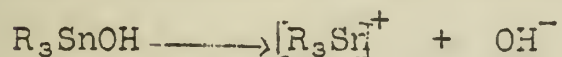
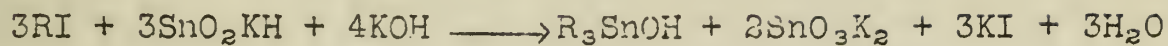
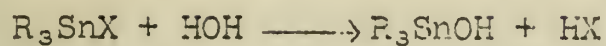
Reactions of stannonic acids and derivatives:



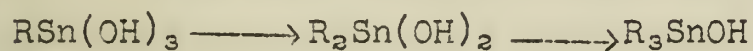
Reactions of stannones:



Formation and reactions of stannols:



The order of decreasing acidity and solubility is:



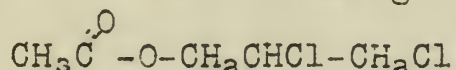
Reported by L. L. Ryden
October 23, 1935.

Bockmüller and Hoffmann

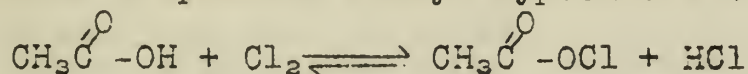
Ann. 519, 165 (1935)

Chem. Inst. of University of Würzburg

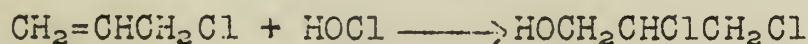
The authors report that chlorination of allyl chloride in glacial acetic acid solution gave the expected 1,2,3-trichloropropane plus a 20 per cent yield of a lower boiling compound which proved to be the following dichloropropyl acetate:



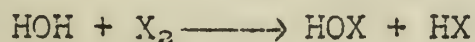
They postulate that there is a reaction between acetic acid and chlorine to produce acetyl hypochlorite,



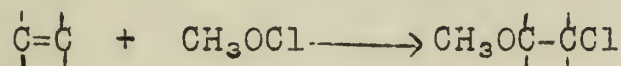
and that in this reaction the equilibrium is shifted far to the left. The acetyl hypochlorite then adds to the allyl chloride in the same manner as hypochlorous acid.



The formation of acyl hypohalites is analogous to the hydrolysis and alcoholysis of halogens,



Methyl and ethyl hypochlorite were first prepared and isolated by Sandmeyer in 1885. They readily add to $>\text{C}=\text{C}<$ systems with the formation of halogenated ethers.



The authors have found that acyl hypohalites are best prepared by the action of halogen on the silver salt of the acid;



An extensive study of the reactions of acyl hypohalites was carried out under the following heads:

1. Oxidizing Power, $\text{RCOOX} + \text{HX} \longrightarrow \text{RCOOH} + \text{X}_2$
2. Spontaneous decomposition, $\text{RCOOX} \longrightarrow \text{RX} + \text{CO}_2$
3. Reaction with water, $\text{RCOOX} + \text{HOH} \longrightarrow \text{RCOOH} + \text{HOX}$
4. Halogenation, $\text{RCOOX} + \text{RH} \longrightarrow \text{RX} + \text{RCOOH}$
5. Addition to C-C double bonds, $\overset{\text{I}}{\underset{\text{I}}{\text{C}}}=\overset{\text{I}}{\underset{\text{I}}{\text{C}}} + \text{RCOOX} \longrightarrow \text{RCOO}\overset{\text{I}}{\underset{\text{I}}{\text{C}}}-\overset{\text{I}}{\underset{\text{I}}{\text{C}}}\text{X}$

Reported by J. H. Brown
October 23, 1935

The Peroxide Mechanism of Kolbe's Hydrocarbon Synthesis

Applied to Monoethyl Adipate

Fichter and Buess, *Helv.* 18, 445 (1935)

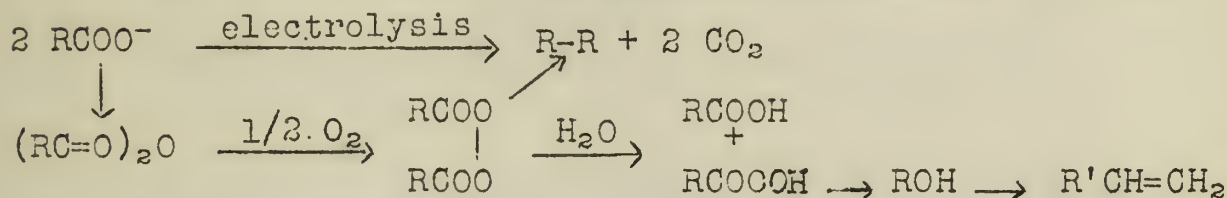
Place: University of Basel, Switzerland.

Previous work: Primarily electro-organic, with special regard to mechanism of Kolbe's hydrocarbon synthesis.

Fichter and his co-workers have been trying to establish the peroxide mechanism of Kolbe's hydrocarbon synthesis since 1918. Briefly, their method of attack has been:

- Synthesis of numerous peroxides,
- Thermal decomposition of these peroxides,
- Comparison of decomposition products with electrolytic products.

The net reaction and Fichter's mechanism follow:



The present paper deals with the above mechanism applied to monoethyl adipate as typical of Fichter's work.

He thermally decomposed monoethyl adipyl peroxide in a steel bomb. From the decomposition product he secured a neutral oil, which was fractionally distilled as follows:

Fraction I (2.5 g.) was found to be a mixture of ethyl n-valerate and ethyl ester of allyl acetic acid.

Fraction II (3.1 g.) was found to be diethyl adipate.

Fraction III (3.0 g.) was found to be diethyl sebacate.

Fraction IV (1.7 g.) was found to be essentially diethyl sebacate.

Fraction V (4.2 g.) was found to be essentially diethyl sebacate.

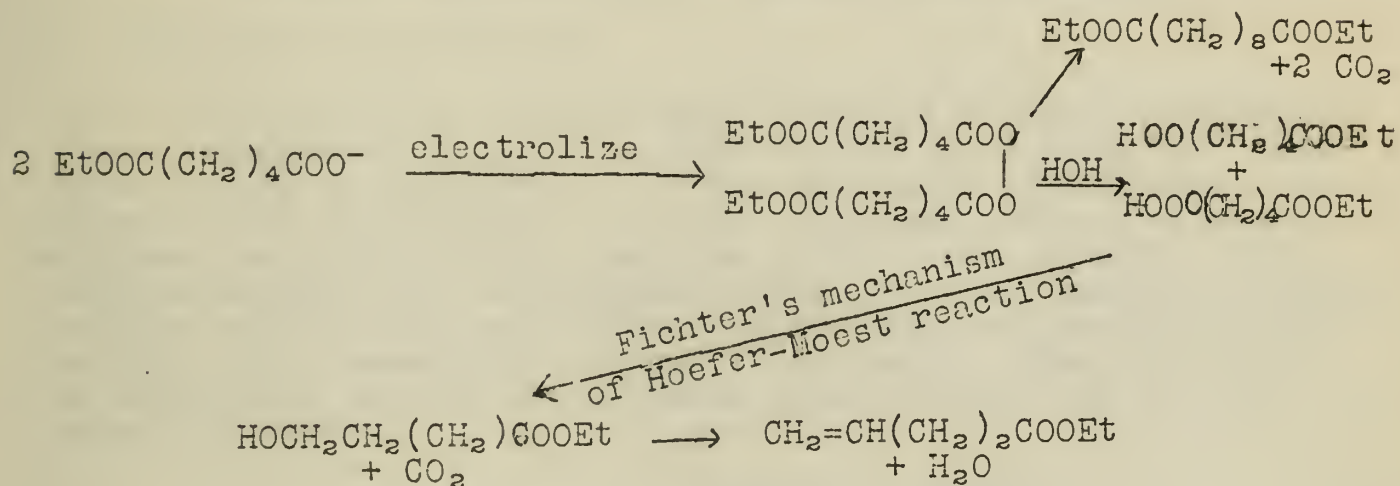
Note that the main product of thermal decomposition of the peroxide was diethyl sebacate (11 g. total), just as it is the main product in the electrolysis of potassium, ethyl adipate. In addition one secures the same unsaturated ester by thermal decomposition as by electrolysis.

Under carefully controlled conditions (high C.D., well cooled anode, proper electrolyte, etc.) the presence of peracid

-2-

(7.22 mg.) and peroxide (13.95 mg.) in the electrolyte was established by titrating the iodine released from KI with $\text{Na}_2\text{S}_2\text{O}_3$.

According to Fichter hydrolysis of the peroxide yields the peracid, which, by loss of CO_2 , accounts for the Hoefer-Moest reaction, and the resulting "alcohol" upon dehydration forms the unsaturated ester, thus:



In view of the establishment of the peroxide and peracid in the electrolyte, and the parallelism of products from thermal decomposition and electrolysis, Fichter concludes that peroxide and peracid must be intermediates to successfully account for all the products of the Kolbe hydrocarbon synthesis.

Reported by Rene Oehler
October 30, 1935.

MECHANISM OF NITRATION

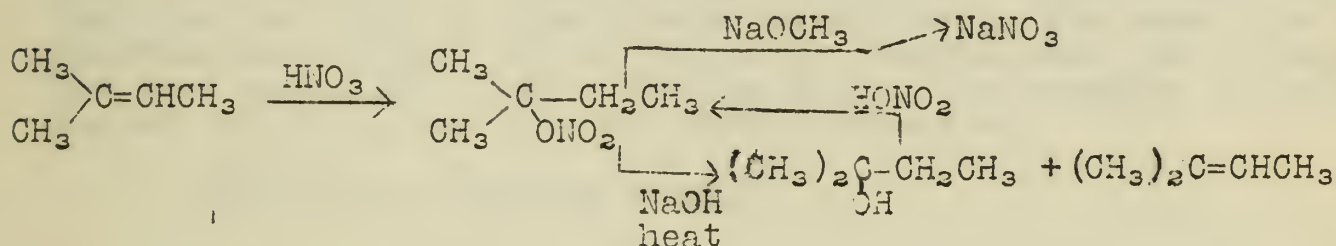
By: A. Michael and G. H. Carlson.
J. Am. Chem. Soc., 57, 1263 (1935)

Place: Harvard University.

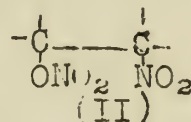
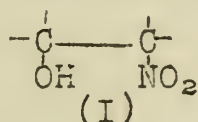
Previous work: Relationship between structure and chemical and physical properties. Acetoacetate ester condensation. Michael condensation.

I. Nitration of Alkylenes:

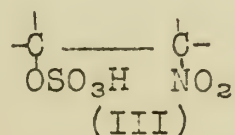
Contrary to the generally accepted nitration mechanism first proposed by Wieland in 1930, nitric acid (98.6 per cent) does not add to alkylenes to yield saturated nitrohydrines or nitro-nitric acid esters. Neither ethylene nor α, α -diphenylethylene react with cold, absolute nitric acid; however, trimethylethylene and isobutylene, being of a more additive nature, combine with nitric acid (absolute or 98.6 per cent) at -20° to form the corresponding nitric acid esters, the structures of which were proved as indicated below in the case of trimethylethylene:



The earlier work of Wieland mentioned above indicated that concentrated nitric acid functioned as $\text{HO} + \text{NO}_2$ when adding to alkylenes to form first a nitrohydrine (I) which was then converted by more nitric acid into a nitro-nitric acid ester (II).



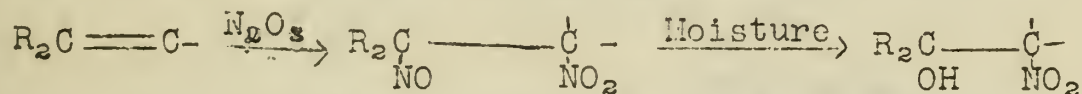
The authors point out that the active nitrating agent used by Wieland was not nitric acid but more probably the mixed anhydride $\text{HOSO}_2\text{ONO}_2$ (formed by the sulfuric acid present), which added to the ethylenic bond to produce a nitro-sulfuric ester (III), and



which in turn could easily undergo substitution by the more negative nitric ester radical to yield the type (II).

101-102-103-104-105-106-107-108-109-110-111-112-113-114-115-116-117-118-119-120-121-122-123-124-125-126-127-128-129-130-131-132-133-134-135-136-137-138-139-140-141-142-143-144-145-146-147-148-149-150-151-152-153-154-155-156-157-158-159-160-161-162-163-164-165-166-167-168-169-170-171-172-173-174-175-176-177-178-179-180-181-182-183-184-185-186-187-188-189-190-191-192-193-194-195-196-197-198-199-200-201-202-203-204-205-206-207-208-209-210-211-212-213-214-215-216-217-218-219-220-221-222-223-224-225-226-227-228-229-230-231-232-233-234-235-236-237-238-239-240-241-242-243-244-245-246-247-248-249-250-251-252-253-254-255-256-257-258-259-260-261-262-263-264-265-266-267-268-269-270-271-272-273-274-275-276-277-278-279-280-281-282-283-284-285-286-287-288-289-290-291-292-293-294-295-296-297-298-299-300-301-302-303-304-305-306-307-308-309-310-311-312-313-314-315-316-317-318-319-320-321-322-323-324-325-326-327-328-329-330-331-332-333-334-335-336-337-338-339-340-341-342-343-344-345-346-347-348-349-350-351-352-353-354-355-356-357-358-359-360-361-362-363-364-365-366-367-368-369-370-371-372-373-374-375-376-377-378-379-380-381-382-383-384-385-386-387-388-389-390-391-392-393-394-395-396-397-398-399-400-401-402-403-404-405-406-407-408-409-410-411-412-413-414-415-416-417-418-419-420-421-422-423-424-425-426-427-428-429-430-431-432-433-434-435-436-437-438-439-440-441-442-443-444-445-446-447-448-449-450-451-452-453-454-455-456-457-458-459-460-461-462-463-464-465-466-467-468-469-470-471-472-473-474-475-476-477-478-479-480-481-482-483-484-485-486-487-488-489-490-491-492-493-494-495-496-497-498-499-500-501-502-503-504-505-506-507-508-509-510-511-512-513-514-515-516-517-518-519-520-521-522-523-524-525-526-527-528-529-530-531-532-533-534-535-536-537-538-539-540-541-542-543-544-545-546-547-548-549-550-551-552-553-554-555-556-557-558-559-560-561-562-563-564-565-566-567-568-569-570-571-572-573-574-575-576-577-578-579-580-581-582-583-584-585-586-587-588-589-590-591-592-593-594-595-596-597-598-599-600-601-602-603-604-605-606-607-608-609-610-611-612-613-614-615-616-617-618-619-620-621-622-623-624-625-626-627-628-629-630-631-632-633-634-635-636-637-638-639-640-641-642-643-644-645-646-647-648-649-650-651-652-653-654-655-656-657-658-659-660-661-662-663-664-665-666-667-668-669-670-671-672-673-674-675-676-677-678-679-680-681-682-683-684-685-686-687-688-689-690-691-692-693-694-695-696-697-698-699-700-701-702-703-704-705-706-707-708-709-710-711-712-713-714-715-716-717-718-719-720-721-722-723-724-725-726-727-728-729-730-731-732-733-734-735-736-737-738-739-740-741-742-743-744-745-746-747-748-749-750-751-752-753-754-755-756-757-758-759-760-761-762-763-764-765-766-767-768-769-770-771-772-773-774-775-776-777-778-779-780-781-782-783-784-785-786-787-788-789-790-791-792-793-794-795-796-797-798-799-800-801-802-803-804-805-806-807-808-809-810-811-812-813-814-815-816-817-818-819-820-821-822-823-824-825-826-827-828-829-830-831-832-833-834-835-836-837-838-839-840-841-842-843-844-845-846-847-848-849-850-851-852-853-854-855-856-857-858-859-860-861-862-863-864-865-866-867-868-869-870-871-872-873-874-875-876-877-878-879-880-881-882-883-884-885-886-887-888-889-890-891-892-893-894-895-896-897-898-899-900-901-902-903-904-905-906-907-908-909-910-911-912-913-914-915-916-917-918-919-920-921-922-923-924-925-926-927-928-929-930-931-932-933-934-935-936-937-938-939-940-941-942-943-944-945-946-947-948-949-950-951-952-953-954-955-956-957-958-959-960-961-962-963-964-965-966-967-968-969-970-971-972-973-974-975-976-977-978-979-980-981-982-983-984-985-986-987-988-989-990-991-992-993-994-995-996-997-998-999-1000-1001-1002-1003-1004-1005-1006-1007-1008-1009-1010-1011-1012-1013-1014-1015-1016-1017-1018-1019-1020-1021-1022-1023-1024-1025-1026-1027-1028-1029-1030-1031-1032-1033-1034-1035-1036-1037-1038-1039-1040-1041-1042-1043-1044-1045-1046-1047-1048-1049-1050-1051-1052-1053-1054-1055-1056-1057-1058-1059-1060-1061-1062-1063-1064-1065-1066-1067-1068-1069-1070-1071-1072-1073-1074-1075-1076-1077-1078-1079-1080-1081-1082-1083-1084-1085-1086-1087-1088-1089-1090-1091-1092-1093-1094-1095-1096-1097-1098-109

Nitric acid (98.6 per cent) does not attack α, α - diphenylethylene at room temperature, but as soon as the reaction mixture is warmed to the point of evolution of nitrous fumes, α, α -diphenyl- β -nitroethyl alcohol is obtained. In fact, all nitration reactions which are not carried out in the cold involve the action of nitrogen tri- and tetroxide. This could account for the formation of the previously mentioned nitrohydrines, thus:

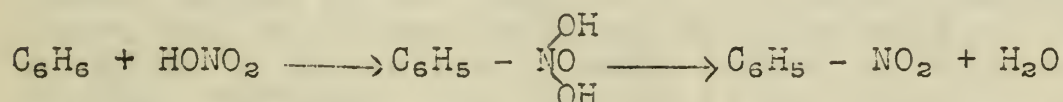


Nitric acid itself does not yield such products, but functions in a normal way to add $H + NO_3$ to alkylenes.

II. Aromatic Nitration:

In support of the $HO + NO_2$ addition theory for the nitration of benzene, Reddelain and Wieland stated that phenanthrene when treated with nitric acid (absolute) gave the ether of 8-hydroxy-9-nitrophenanthrene. The present authors claim the formation of this compound to be another case of the action of the oxides of nitrogen on a double bond linkage, in view of the fact that they obtained a phenanthrene nitric acid ester when the same reaction was carried out in the cold. Furthermore, it is pointed out that according to the addition theory for aromatic nitration, benzene should yield tri- not mononitrobenzene.

Michael and Carlson propose,



for the mechanism of aromatic nitration, in which the first step proceeds by the common aldolization reaction.

Reported by Marlin T. Leffler
October 30, 1935.

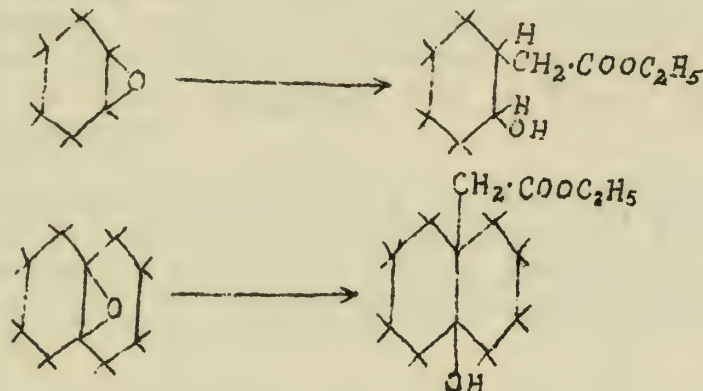
THE UNIVERSITY OF CHICAGO

B. Arbusow

Ber., 68, (8), 1430-1438 (1935)

Butlerow Institute of Kasan, U.S.S.R.

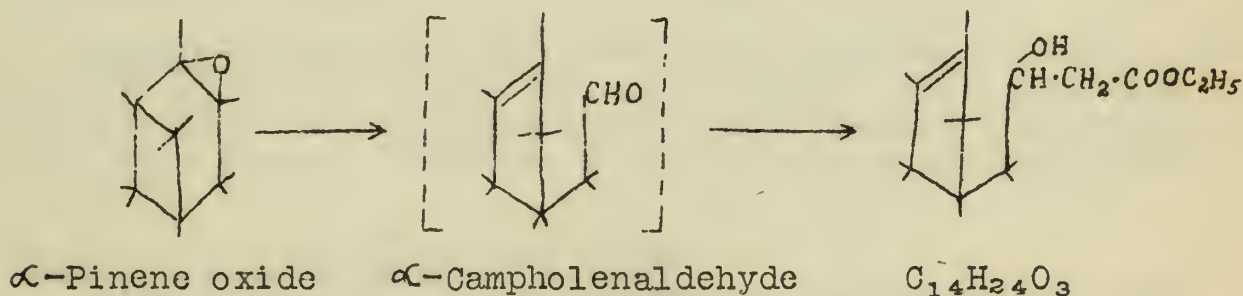
The action of ethyl bromoacetate and zinc on cyclohexene oxide and on 9,10-octalin oxide has been shown to yield the following products:



From these facts the normal product of the reaction of ethyl bromoacetate and zinc on α -pinene oxide would be expected to be the saturated ester:



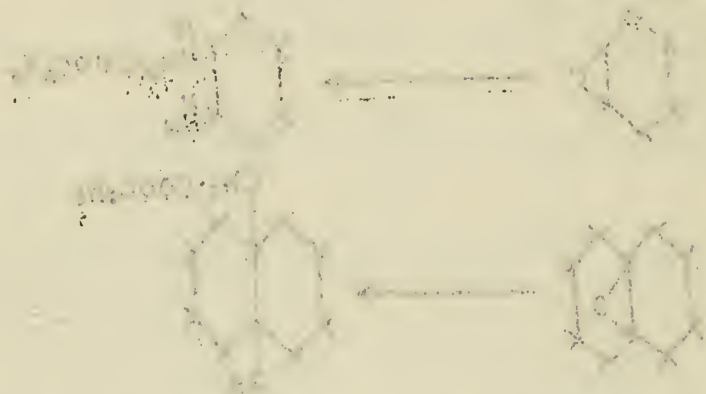
However, there was actually obtained an unsaturated ester, $\text{C}_{14}\text{H}_{24}\text{O}_3$, which is identical with that produced by the direct action of the reagents on α -campholenaldehyde. It is shown that α -pinene oxide may be rearranged to α -campholenaldehyde by the action of small amounts of zinc bromide. Evidently, therefore, the reaction is not directly on the α -pinene oxide but on the product produced by the isomerization with traces of zinc bromide present.



Mechanisms are offered for the rearrangement of α -pinene oxide to α -campholenaldehyde and the production of α -campholenaldehyde is verified by oxidation to α -campholenic acid by silver oxide and thence to dihydroxy- α -campholenic acid by potassium permanganate.

2. The compound 4-picenoic acid, which is a solid at room temperature, is a dimer of 4-picenoic acid. It is a dimer of 4-picenoic acid, which is a solid at room temperature. It is a dimer of 4-picenoic acid, which is a solid at room temperature.

The action of 4-picenoic acid on 4-picenoic acid is a dimerization reaction. The action of 4-picenoic acid on 4-picenoic acid is a dimerization reaction. The action of 4-picenoic acid on 4-picenoic acid is a dimerization reaction.



From these facts the correct structure of the reaction of 4-picenoic acid and 4-picenoic acid is a dimerization reaction. From these facts the correct structure of the reaction of 4-picenoic acid and 4-picenoic acid is a dimerization reaction.



However, there was a small amount of 4-picenoic acid ester, 4-picenoic acid, which is a solid at room temperature. However, there was a small amount of 4-picenoic acid ester, 4-picenoic acid, which is a solid at room temperature. However, there was a small amount of 4-picenoic acid ester, 4-picenoic acid, which is a solid at room temperature.



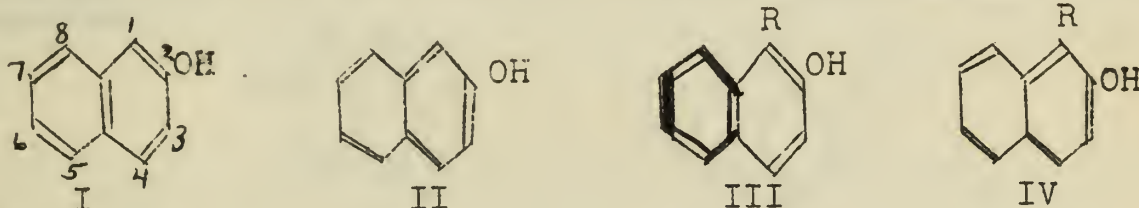
4-Picenoic acid 4-Picenoic acid 4-Picenoic acid

Molecular weight of 4-picenoic acid is 254. Molecular weight of 4-picenoic acid is 254. Molecular weight of 4-picenoic acid is 254. Molecular weight of 4-picenoic acid is 254. Molecular weight of 4-picenoic acid is 254.

L. F. Fieser and W. C. Lothrop
Harvard University
J. Am. Chem. Soc., 57, 1459, (1935)

It has long been known that the anomalous reactions of the naphthalene nucleus are unexplainable on the assumption of two condensed aromatic rings with oscillating bonds. This review indicates that the bonds of naphthalene differ from those of benzene only in their mobility and in their reactivity or degree of unsaturation.

Early attention was called to the difference in the behavior of the (1) and the (3) positions of β -naphthol and β -naphthyl amine, i.e., the "ortho" positions. These differences are most easily understandable by a fixed condition of the bonds.



1. Nuclear Substitution

a. Coupling reaction.—All mechanisms require a double bond between the hydroxyl and the entering position. Diazonium salts couple at (1), indicating formula I rather than II.

1-Alkyl-2-naphthol will not couple. Since IV should couple, III is evidently the correct representation of β -naphthol.

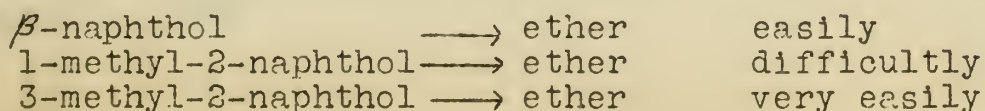
b. Allyl ether rearrangement.—This involves a 1,3 shift, and requires a double bond. β -Naphthol allyl ethers easily rearrange to 1-allyl-2-naphthols. The allyl group never rearranges to the (3) position.

Furthermore, if position (1) is filled, rearrangement will not occur. Formulae I and III are indicated.

c. Skraup's reaction.—This reaction requires a double bond in order to proceed. β -Naphthylamine always closes the ring in position (1). If this position is substituted, the reaction will not take place. Formulae I and III are again preferable to II and IV.

2. Reaction of the functional group

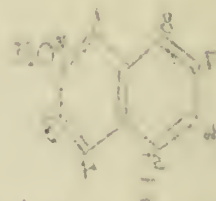
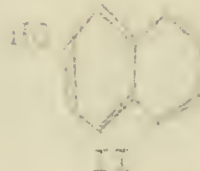
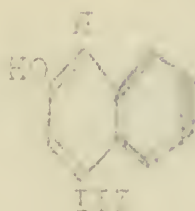
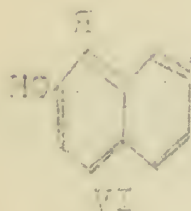
a. Etherification.—Henry's mechanism indicates that the general reaction of esterification requires addition to a double bond followed by a splitting out of water. The replacement of the H by an R group on the double bond involved should retard the reaction. Treatment with methyl alcohol and dry hydrogen chloride resulted in the following reactions:—



D. F. STEVENSON & W. C. LATHROP
 University of California
 3. Am. Chem. Soc., 57, 1155 (1935)

It has long been known that the naphthalene reactions of the
 substituted naphthalenes are unsymmetrical and the question is
 constantly arising as to which is the reactive center. This review
 indicates that the center of reactivity is not fixed but
 depends only on their mobility and in their reactivity on the
 type of substitution.

Early attention was called to the difference in the re-
 activity of the (1) and the (2) positions of 6-naphthol and
 2-naphthyl amine, i.e., the "ortho" positions. These differ-
 ences are most easily understandable by a fixed position of
 the bonds.



1. Naphthalene Substitution

a. General reaction—All naphthalene reactions require a double bond
 between the naphthyl and the substituent. Reaction I, however,
 exists couple at (1), indicating formula I rather than II.

1-Allyl-6-naphthol will not couple. Since IV should
 couple, III is evidently the correct representation of
 6-naphthol.

b. Allyl ether rearrangement—This involves a 1,3 shift
 and requires a double bond. 6-Naphthol allyl ether easily
 rearranges to 2-allyl-6-naphthol. The allyl group never re-
 arranges to the (2) position.

Furthermore, if position (1) is filled, rearrangement
 will not occur. Formulas I and II are indicated.

c. General reaction—This reaction requires a double bond
 in order to proceed. A 1,3 shift always closes the ring
 in position (1). If this position is substituted, the reaction
 will not take place. Formulas I and II are again indicated
 as II and IV.

2. Reaction of the Naphthalene Ring

a. Substitution—Many naphthalene reactions that re-
 quire a double bond in the naphthalene ring are indicated to
 couple and followed by a shifting out of water. The reaction
 must be the R by an R group on the double bond involved should
 retard the reaction. Treatment with methyl alcohol and dry
 hydrogen chloride resulted in the following reactions:

6-naphthol ———> 1-allyl-6-naphthol ———> 2-allyl-6-naphthol

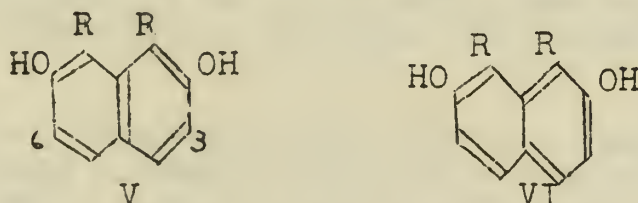
The two latter reactions indicate that the effect is not ortho steric hindrance, but is rather steric hindrance of the double bond between positions (1) and (2).

3. Halogenation.-Evidence of the immobility of the double bond.

Treatment of 1-chloro-2-naphthol with bromine results in the formation of a 1-bromo-1-chloro-2-keto derivative with a quinonoid structure, rather than the 1,3-dihalogen compound which would be expected if a shift of double bonds could take place.

4. Failure to form 2,3 quinones.-1,2-dihydroxy-naphthalene forms an ortho quinone, whereas the 2,3 isomer does not. The formation of a quinone from a dihydroxy compound requires a double bond between the hydroxyls.

5. Establishment of the points of unsaturation in the rest of the molecule.



Because of the position of the double bonds, V should be incapable of substitution at positions (3) and (6). VI should be substituted at (3).

Actually, the substituted dihydroxy-naphthalenes do not couple with diazonium compounds, nor do their allyl ethers rearrange. This indicates the symmetrical formula, V, as the correct one.

6. Ease of reduction of one ring, and the activity of the α -position.-The valence claim made on the double bond between the two rings makes one ring less aromatic and more unsaturated, or aliphatic than the other. This would make naphthalene somewhat analagous to a 1,4 conjugated system with both ends connected to the same ring. It should show the reactions of $C_6H_5-CH=CH-CH=CH-C_6H_5$. The 1,4 conjugated positions of this compound correspond to the (1) and (4), or α -positions of naphthalene, and account for the ease of reduction, and the reactivity of the α -position to halogenation, nitration, and other reactions.

Fries suggests that the tendency for both rings to remain aromatic suppresses oscillation of the bonds.

Reported by Harry H. Weinstock, Jr.
November 9, 1935

The first stage of the investigation was the determination of the nature of the substance, which was found to be a solid, white, crystalline material, soluble in water and alcohol.

The second stage of the investigation was the determination of the molecular weight of the substance, which was found to be 180. This was determined by the method of Dumas, which involves the measurement of the volume of gas evolved from a known weight of the substance.

The third stage of the investigation was the determination of the structure of the substance, which was found to be a diatomic molecule, consisting of two atoms of the same element, bonded together by a single bond.

The fourth stage of the investigation was the determination of the physical properties of the substance, which were found to be: melting point, 100°C; boiling point, 180°C; density, 1.8 g/cm³.



The fifth stage of the investigation was the determination of the chemical properties of the substance, which were found to be: it is a weak acid, reacting with bases to form salts; it is a weak oxidizing agent, reacting with reducing agents to form the corresponding reduced form.

The sixth stage of the investigation was the determination of the synthesis of the substance, which was found to be: it can be synthesized by the reaction of two atoms of the same element, each in a +1 oxidation state, to form a diatomic molecule.

The seventh stage of the investigation was the determination of the uses of the substance, which were found to be: it is used as a reagent in the synthesis of organic compounds, and as a catalyst in the oxidation of organic compounds.

H. Sutter and N. Wijkmann

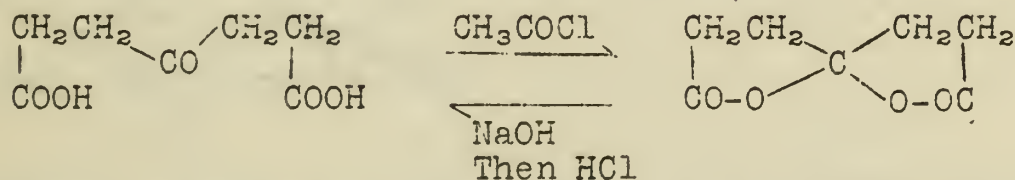
Ann., 519, 97 (1935)

Chem. Laboratorium der Bayer, Akademie
der Wissenschaften, MunichPrevious work:- Sutter - Oxidase, peroxidase
Wijkmann, Compounds formed by molds.

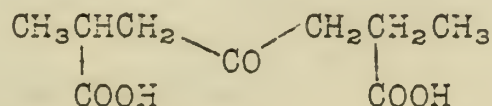
Two substances which can be isolated from mold cultures, $C_{18}H_{20}O_7$ and $C_{12}H_{20}O_6$, are known as glauconic acid I and II, or glauconic acid and glaucanic acid. Glauconic acid on heating undergoes degradation, $C_{18}H_{20}O_7 \rightarrow C_{11}H_{12}O_6 + C_7H_{12}O$. $C_7H_{12}O$ has been shown to be α, β -diethyl acrolein. The other fragment whose constitution is under investigation, is called glauconin.

Glauconin, on treatment with HCl in a sealed tube, yields an acid mixture and a small amount of a neutral substance, $C_9H_{12}O_4$, m.p., 144° . $C_9H_{12}O_4$ reacts with 2 moles of NaOH. When this is neutralized with HCl a dicarboxylic acid is obtained which, on treatment with CH_3COCl regenerates $C_9H_{12}O_4$. The acid mixture, after treatment with CH_3COCl , may be fractionally crystallized into three compounds, all with formula $C_9H_{12}O_4$, but m.p. 116° , 126° , 144° . Last is identical with 144° above. 126° and 144° with NaOH and then HCl yield the same dicarboxylic acid, m.p. 140° ; 116° yields dicarboxylic acid, m.p. 127° .

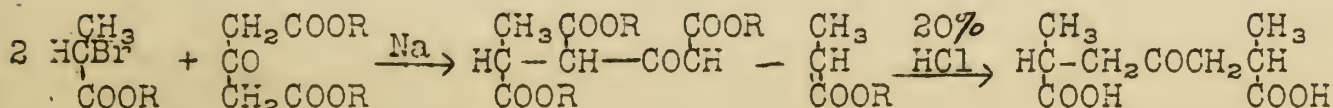
Hydrochelidonic acid, studied by Volhard, has similar reactions.



Its absorption spectra and that of 140° are similar. 140° has 2 CH_2 groups more than hydrochelidonic, and since on HNO_3 oxidation, pyrotartaric acid is formed, there must be two methyl groups substituted on the hydrochelidonic residue. Absorption spectra studies favor:-



It was synthesized according to the following scheme:-



On the Constitution of Glucosonic Acid

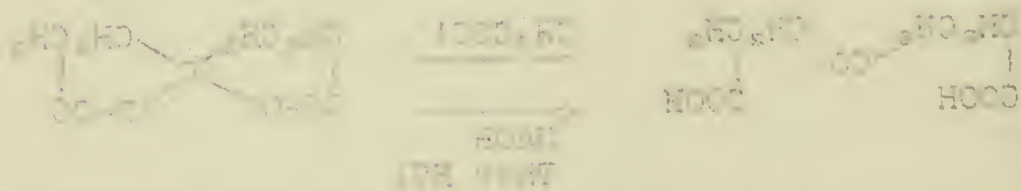
By G. S. Whitby and H. W. Williams
 (Received 1932, 27 June)
 Department of Chemistry, University of Liverpool, England

Previous work: Whitby and Williams, *Chemical Communications*, 1931, 101.
 Williams, *Chemical Communications*, 1931, 101.

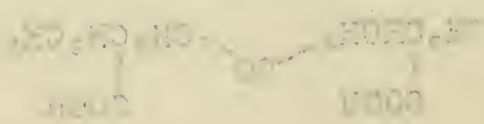
Two substances which can be isolated from milk whey, Glucose and Glucosonic acid, are known as glucosonic acid I and II. On oxidation with potassium dichromate, Glucosonic acid on heat-
 ing undergoes dehydration, $C_6H_{12}O_6 \rightarrow C_6H_{10}O_5 + H_2O$.
 Glucose has been shown to be a polyhydroxy aldehyde. The other
 isomer whose constitution is under investigation is called
 Glucosonic.

Glucosonic, on treatment with HCl in a sealed tube, yields
 an acid mixture and a small amount of a neutral substance,
 $C_6H_{12}O_6$, $C_6H_{10}O_5$, $C_6H_{12}O_6$ reacts with HCl to form
 When this is neutralized with $NaOH$ a mixture of acids is ob-
 tained which, on treatment with $CaCl_2$, gives a mixture of
 The acid mixture, after treatment with $CaCl_2$, may be
 fractionally crystallized into three components, all with for-
 mula $C_6H_{12}O_6$, but m.p. 115°, 120°, 125°. Last is identical
 with 145° above. 120° and 125° with $NaOH$ and then HCl yields
 the same dihydroxylic acid, m.p. 120°: 125° yields dihydroxylic
 acid, m.p. 125°.

Hydroxylic acid, isolated by Williams, see similar
 reaction.



The absorption spectra and heat of 125° are similar. 120° and
 125° groups were then hydroxylic acid, and also on the
 oxidation, hydroxylic acid is formed, there was no
 methyl group attached to the hydroxylic acid
 Absorption spectra similar to:-

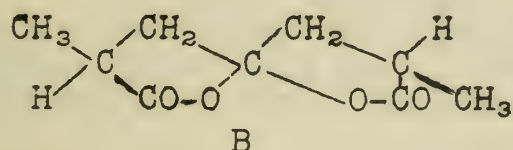
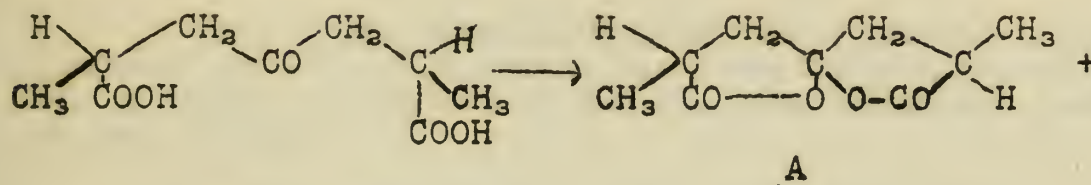


It was synthesized according to the following scheme:-

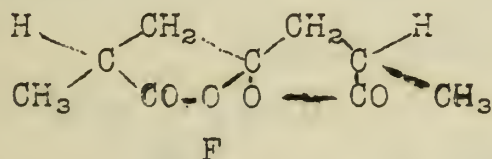
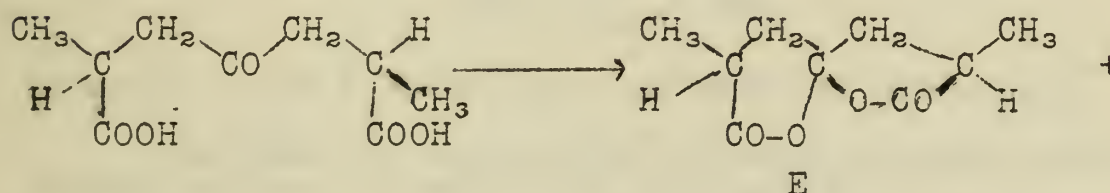
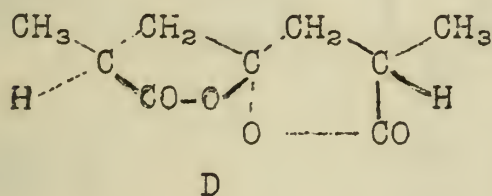
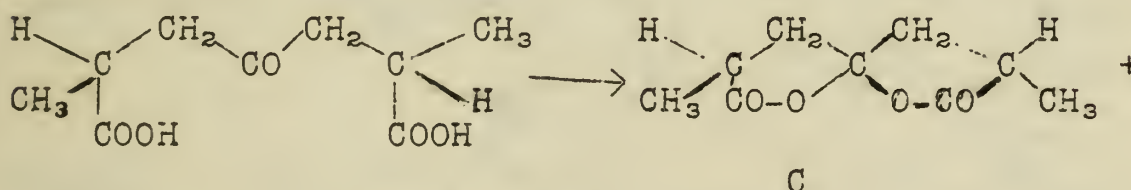


One meso and two active acids are possible, and correspondingly six lactones. 127° is the meso acid; 140° is the racemic.

Meso



Racemic

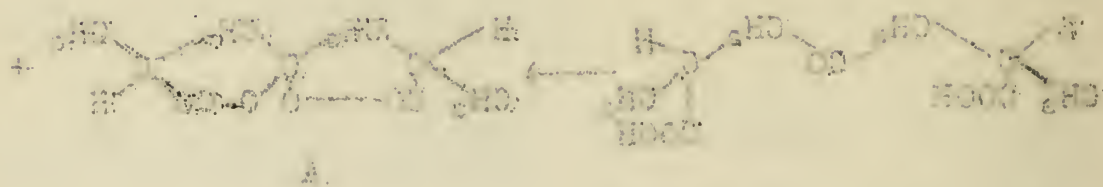


The three racemate lactones, AB, CD, and EF were prepared and identified with those isolated from glauconin by mixed melting point determinations. No formulae are as yet proposed for glauconin or glauconic acid.

Reported by Lillian H. Meyer
November 13, 1935.

The more and the active side are possible, and the reaction is the reaction. The more and the active side are possible, and the reaction is the reaction.

Figure



A

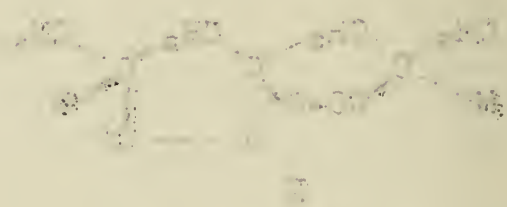


B

Figure



C



D



E



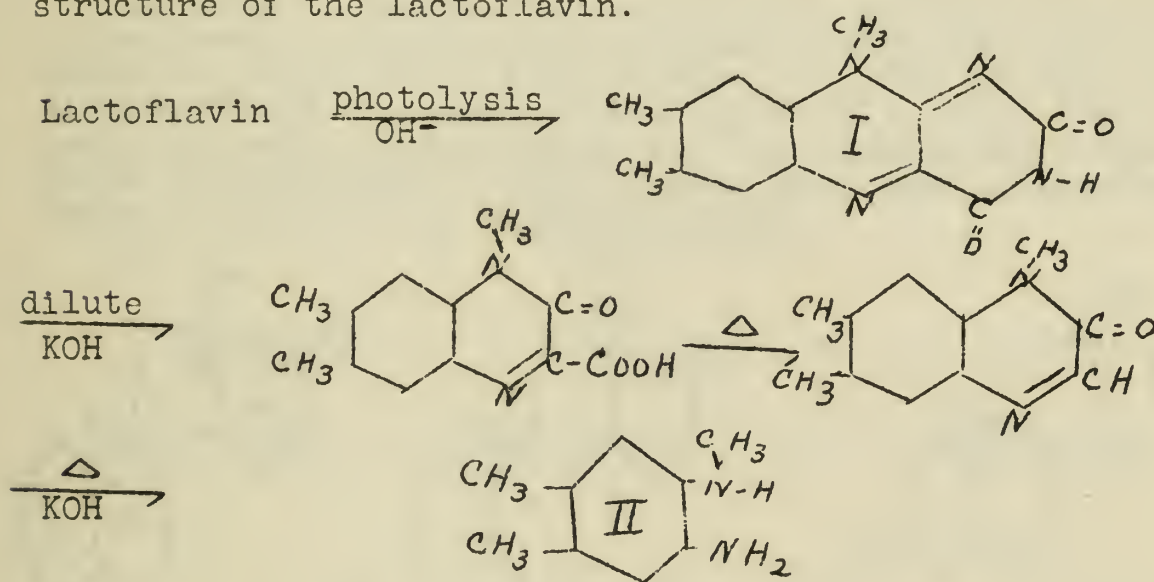
F

The more and the active side are possible, and the reaction is the reaction. The more and the active side are possible, and the reaction is the reaction.

Richard Kuhn and others
Kaiser-Wilhelm Institute, Heidelberg
Ber., 68, 1768 (1935)

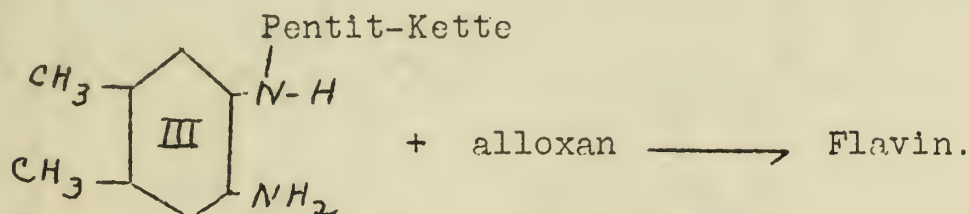
Since 1926, when Goldberger discovered vitamin B₂, an enormous amount of research has been undertaken to determine the chemical constitution and the physiological characteristics of the vitamin.

In 1933, the work on chemical structure was given a great impetus by the isolation of pure vitamin B₂. The degradation of this pure vitamin gave an insight into the actual structure of the lactoflavin.



Products I and II have been confirmed by synthesis.

In 1934, by condensing III with alloxan both Kuhn and Karrer obtained vitamin-like substances.

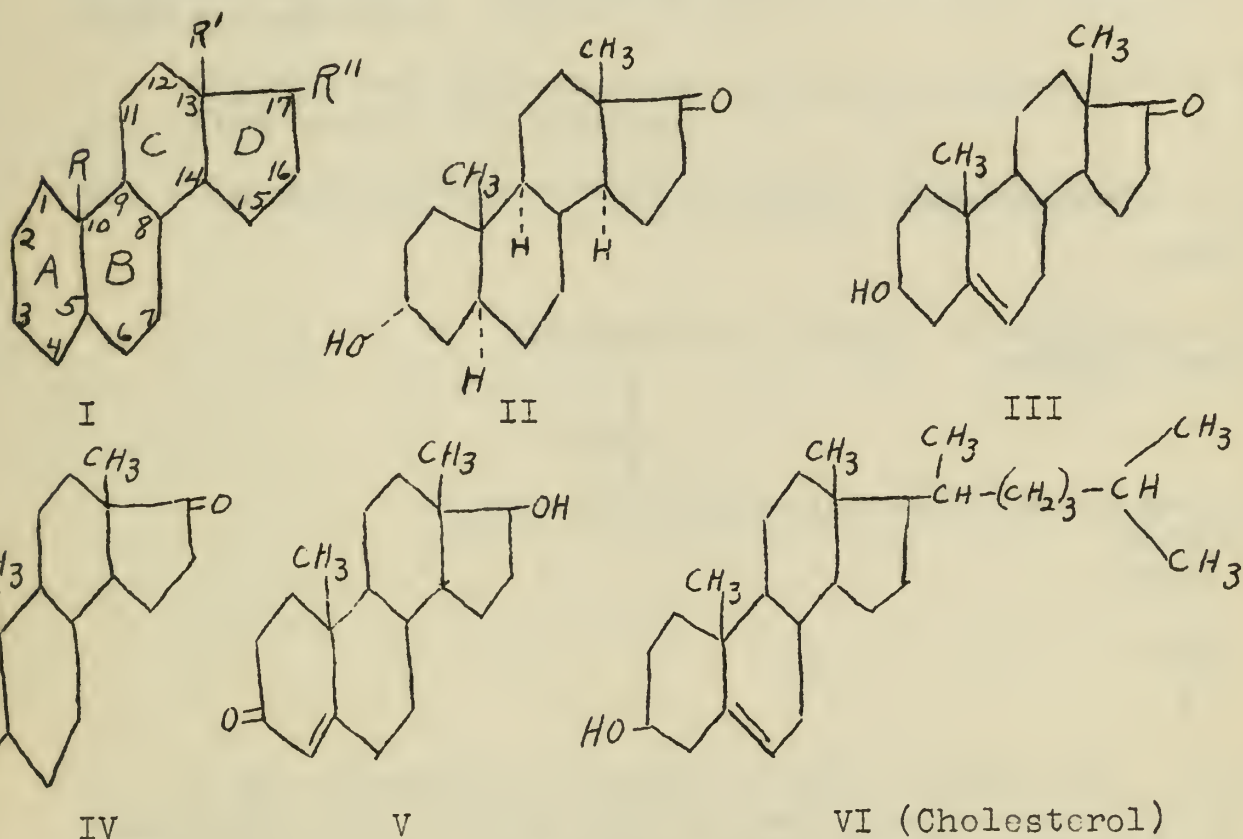


The only part of the structure remaining to be established was the configuration of the sugar side-chain (Pentit-Kette). This part was accomplished by the synthesis of 6,7-dimethyl riboflavin which is identical with the natural vitamin in physical, chemical, and physiological properties.

(Androstene-3-one-17-ol)

L. Ruzicka and A. Wettstein
Helv., 18, 1264 (1935)
Zurich, Organisches Chemisches Laboratorium
der Eidg. Technisches Hochschule and
Basel, Wissenschaftliche Laboratorien der
Gesellschaft für Chemische Industrie,
Pharmazeutische Abteilung

In 1934 L. Ruzicka and assistants oxidized the four stereoisomeric dihydrocholesterols to the corresponding four forms of 3-hydroxy-17-keto-cholane.^{1,2} One of these isomers, 3-*epi*-hydroxy-etio-allo-cholanone-17 (II), they found to be identical with the purified male sex hormone extracted from urine by Butenandt.³ This hormone was named androsterone. Chromic acid was the oxidizing agent.



I is the type formula of the cholane group with the numbering system.

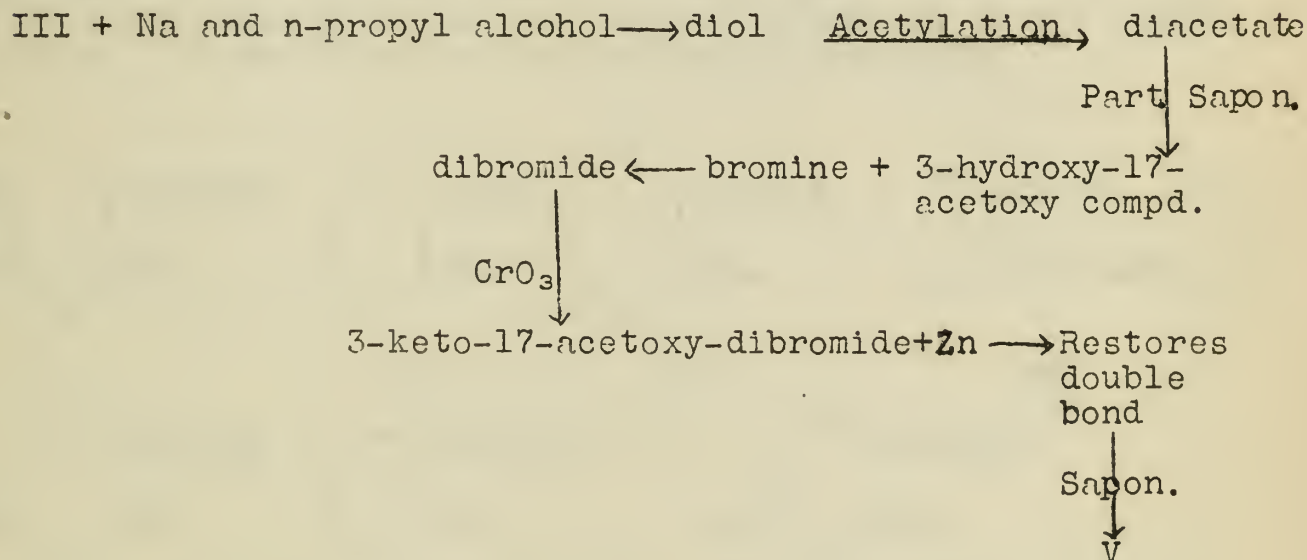
In July 1935 Ruzicka and A. Wettstein reported the oxidation of cholesterol to trans-dehydro-androsteron (III), protecting the hydroxyl group and double bond from oxidation

by acetylation and addition of bromine.⁴ III was found to be physiologically active by the capon comb growth test and was identified as the unsaturated hydroxy-ketone, $C_{19}H_{28}O$, isolated by Butenandt and Dannenbaum from urine.⁵

III was oxidized further to androstene-dione (IV), which was a little less active in the capon comb growth test than was androsterone itself.

From the observation that a sample of testicular extract concentrate was much more active in rat tests than was a sample of urine extract concentrate of equal activity in the capon comb growth test, Ruzicka reasoned that testicular extracts must contain a hormone more active in the rat test than either androsterone or trans-dehydro-androsterone, which were the only active compounds extracted from urine. Furthermore, the hormone activity of the testicular extracts could be destroyed by treatment with alkali which is not the case with urine extracts, since androsterone and trans-dehydro-androsterone are alkali stable. Ruzicka postulated that this alkali unstable hormone must be an α, β -unsaturated ketone identical with IV or with 3-keto-17-hydroxy-androstene (V).

Ruzicka and Wettstein succeeded in preparing V by the following series of reactions:



V was identified by means of m.p., mixed m.p., absorption band, m.p. of derivatives, and hormone activity as testosterone found by various workers in testicular extracts.

1. Helv., 17, 1389, (1934)
2. Helv., 17, 1395, (1934)
3. Naturwissenschaften, 21, 54, (1933)
4. Helv., 18, 986, (1935)
5. Z. Phys. Chem., 239, 192, (1934)

Reported by G. A. Nesty
November 20, 1935

Notes

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11. 11. 11

1

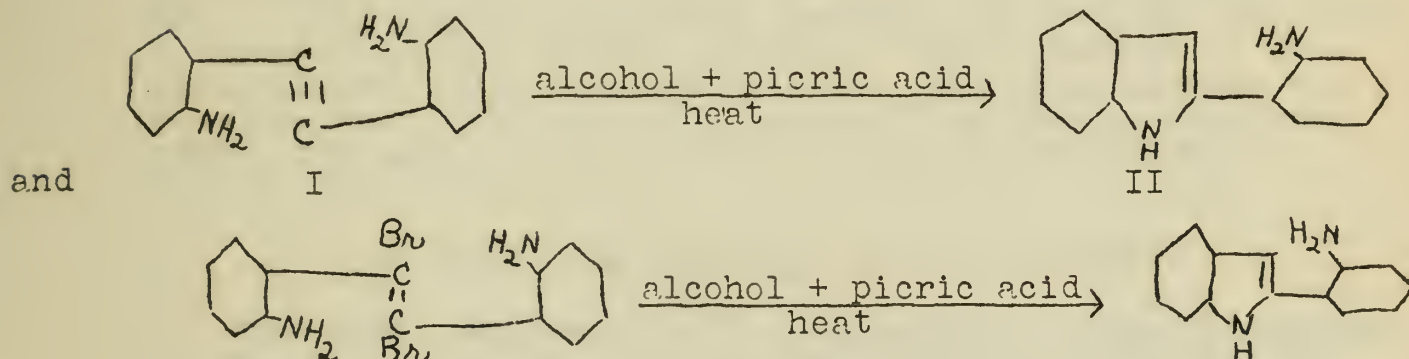
1125

37

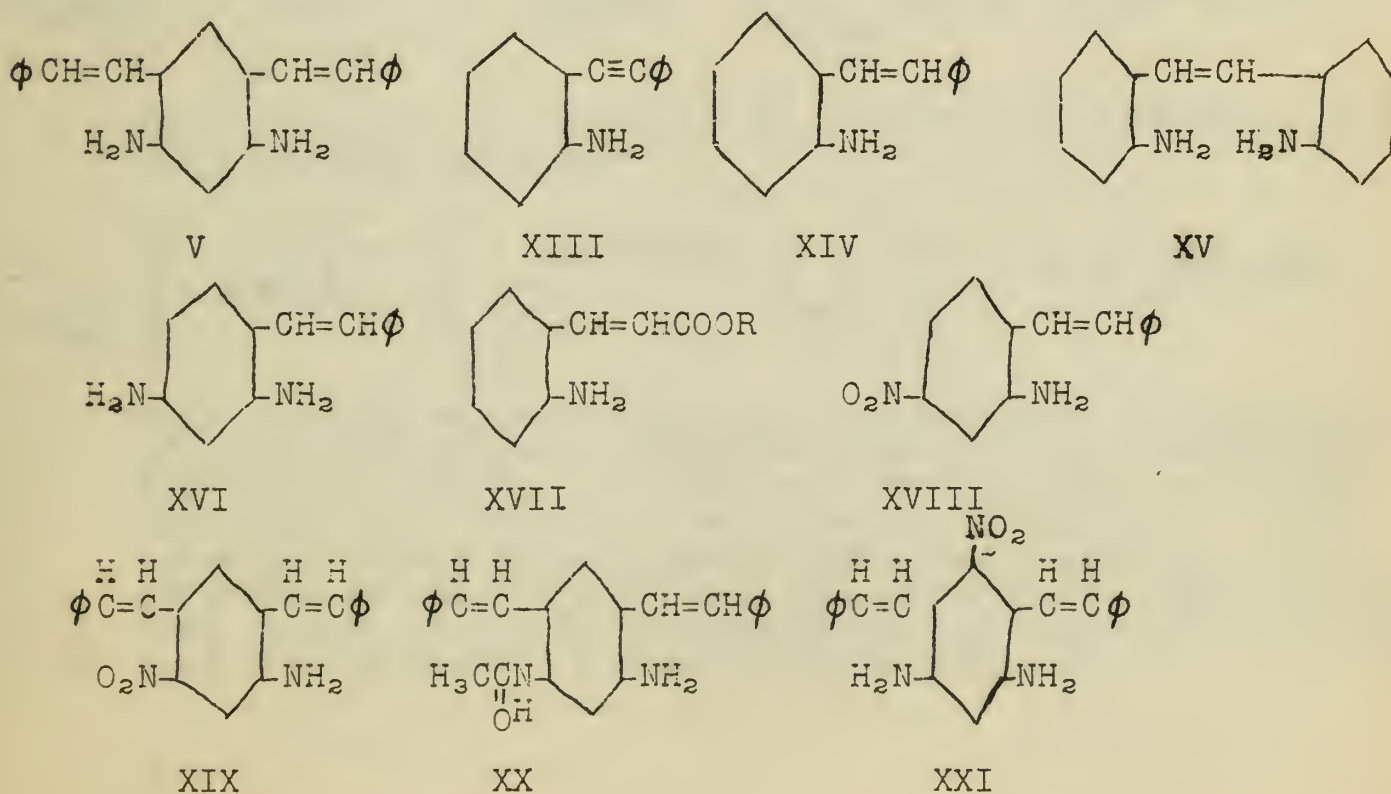
Rearrangement respectively of *o*-aminated Tolans and Stilbenes into Derivatives of Indol and Indolin. Also Concerning the Aminated Double Stilbenes.

Ruggli and Schmidt, *Helv.*, 18, 1215-1229(1935)
University of Basel

Previously Ruggli had observed that *o,o'*-diamino-tolan rearranged into 2-(*o*-aminophenyl)-indol when heated with alcoholic picric acid solution.



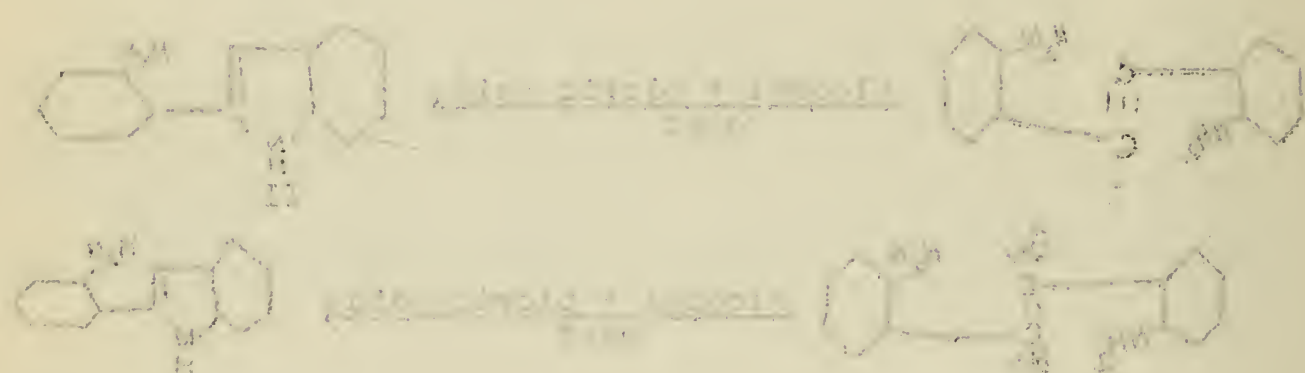
The purpose of this work was to investigate the use of this mild ring-closing medium for further syntheses in the indole series. It was tried on the following compounds:



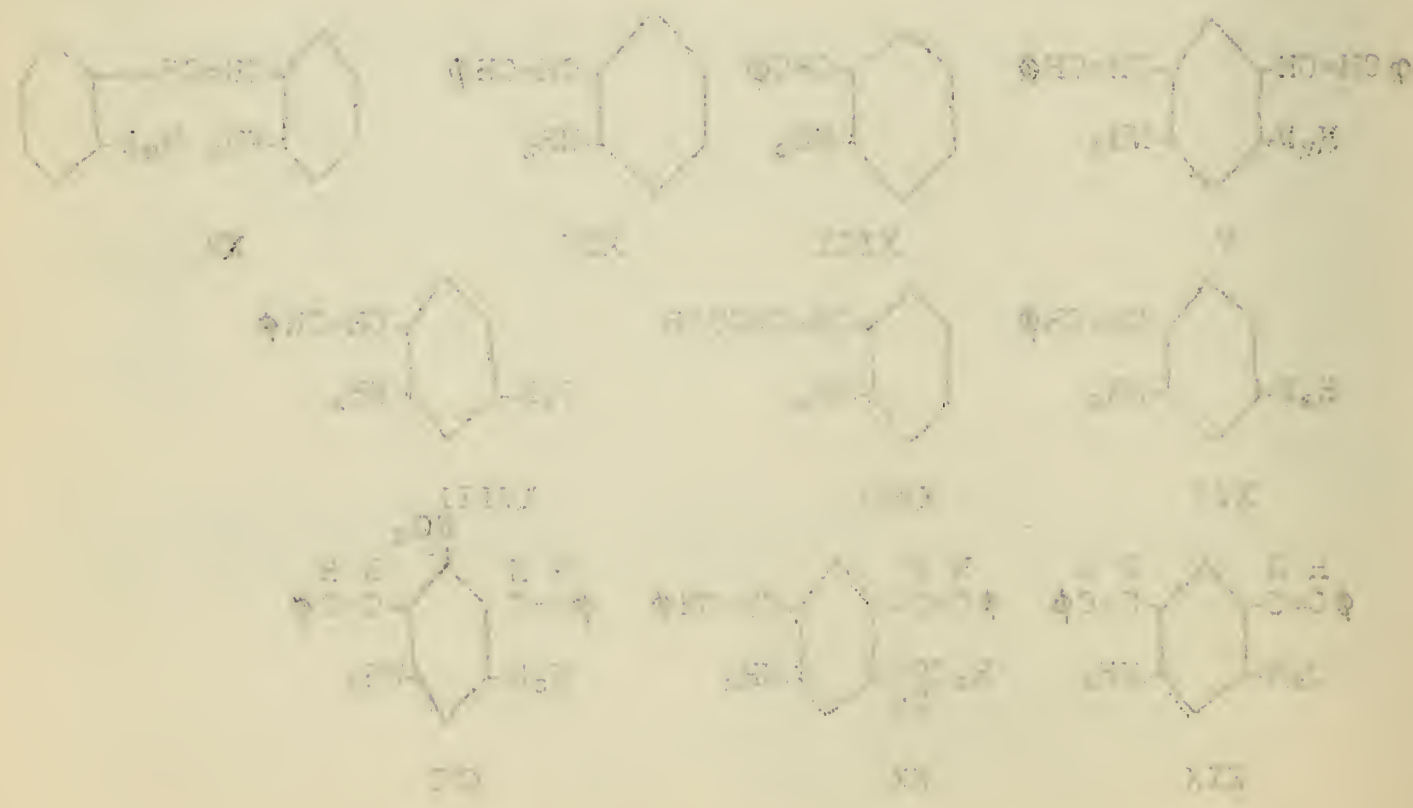
Reaction of 2-substituted 1,4-dioxane-5-carboxylic acids with 1,4-dioxane-5-carboxylic acid. The reaction was carried out in 1,4-dioxane at 100°C for 24 hours.

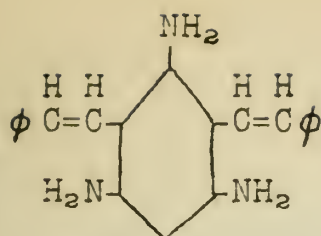
Yield: 85% (based on 1,4-dioxane-5-carboxylic acid).
 mp: 105-106°C (decolor).
 IR (KBr): 1715 (C=O), 1600 (C=C), 1510 (C=C), 1450 (C=C), 1380 (C=C), 1320 (C=C), 1280 (C=C), 1240 (C=C), 1180 (C=C), 1140 (C=C), 1100 (C=C), 1060 (C=C), 1020 (C=C), 980 (C=C), 940 (C=C), 900 (C=C), 860 (C=C), 820 (C=C), 780 (C=C), 740 (C=C), 700 (C=C), 660 (C=C), 620 (C=C), 580 (C=C), 540 (C=C), 500 (C=C), 460 (C=C), 420 (C=C), 380 (C=C), 340 (C=C), 300 (C=C), 260 (C=C), 220 (C=C), 180 (C=C), 140 (C=C), 100 (C=C).

Elemental analysis: Calcd for C₁₂H₁₈O₄: C, 66.67%; H, 8.89%; O, 24.44%. Found: C, 66.5%; H, 8.8%; O, 24.5%.

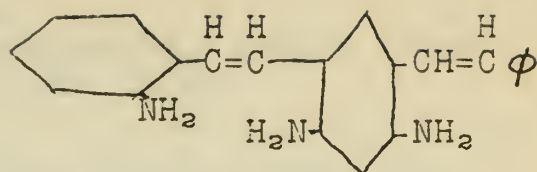


The purpose of this work was to investigate the reaction of 1,4-dioxane-5-carboxylic acid with 1,4-dioxane-5-carboxylic acid. The results are given in the following table:





XXII

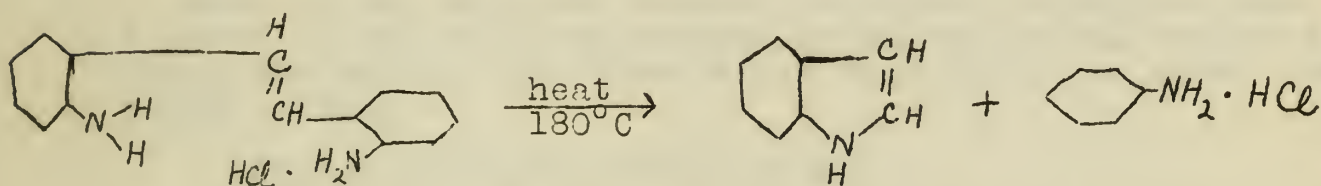


XXIII

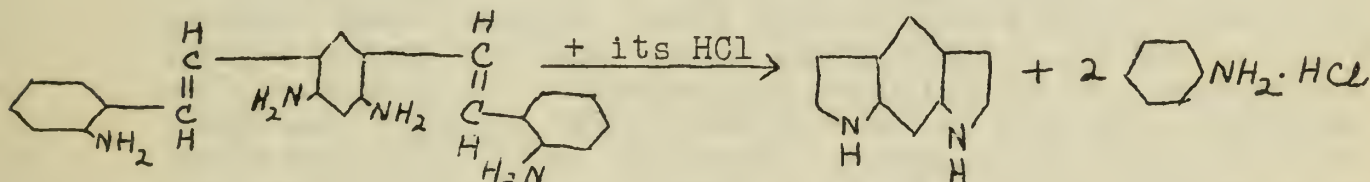
A rearrangement was obtained only with the compounds V and XVI. 1,3-distyryl-4,6-diamino benzene (V) gave the expected 1-phenyl-5-styryl-6-amino indolin. The structure of this indolin derivative was established. The same indolin derivative was obtained in the case of 2,4-diamino-stilbene (XVI). No explanation for its formation was offered.

Concerning the Aminated Double Stilbenes

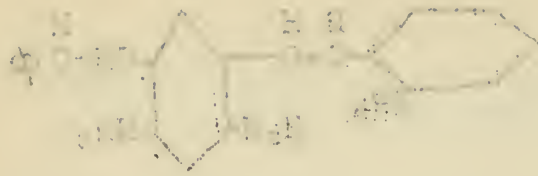
The indol synthesis of J. Thiele and O. Dimroth depends on the fact that dry o,o'-diamino-stilbene mixed with an equivalent amount of its dry dihydrochloride with heating decomposes as follows:



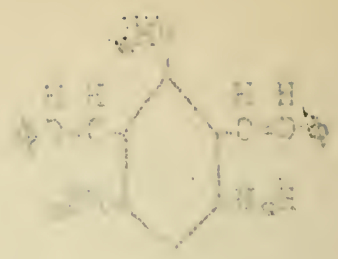
Using this type of synthesis the authors had intended to try the following synthesis:



This starting material could not be prepared. The synthesis of the double stilbene was tried starting with 1,3-distyryl-4,6-diamino benzene. In this case two molecules of benzene must split out instead of two molecules of aniline. A new amine was formed but not the desired double stilbene. The structure of the new amine was not established. This type of ring closure was tried on several similar compounds, but in no case was the desired double stilbene obtained.



XIII



XIV

A reaction of compound XIII with the compound V and
 XVI: 6,8-dihydro-4,5-dioxo-1,2,3,4-tetrahydropyridine
 (XVI) was obtained. The structure of this
 product is shown in the scheme. The compound
 is a dimer of the starting material. The structure
 is shown in the scheme. The compound is a dimer
 of the starting material. The structure is shown
 in the scheme. The compound is a dimer of the
 starting material. The structure is shown in the
 scheme. The compound is a dimer of the starting
 material. The structure is shown in the scheme.
 (XVI)

Converting the double bond in the molecule

The double bond in the molecule of 1,2,3,4-tetrahydropyridine
 was converted into a single bond by the reaction
 of the compound with the compound V and XVI.
 The structure of the product is shown in the
 scheme. The compound is a dimer of the starting
 material. The structure is shown in the scheme.
 The compound is a dimer of the starting material.
 The structure is shown in the scheme.



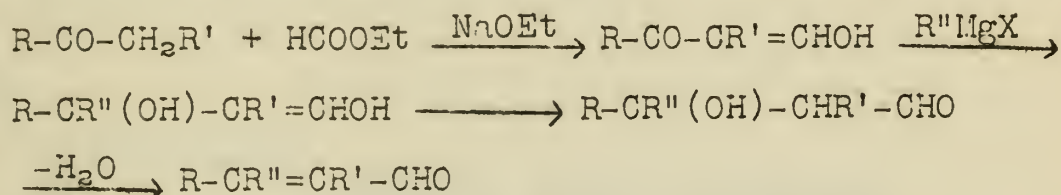
Using this type of synthesis the authors had obtained the
 following compounds:



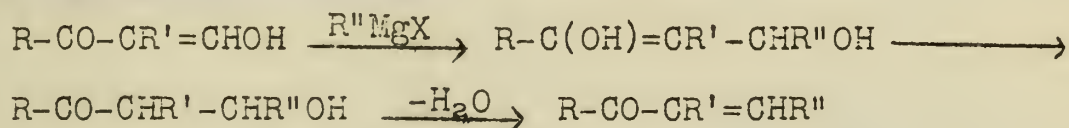
This reaction scheme could not be improved. The synthesis
 of the double bond was tried starting with 1,2,3,4-tetrahydropyridine
 and 6,8-dihydro-4,5-dioxo-1,2,3,4-tetrahydropyridine (XVI).
 In this case two molecules of the starting material
 were used. The structure of the product is shown in the
 scheme. The compound is a dimer of the starting material.
 The structure is shown in the scheme. The compound is a
 dimer of the starting material. The structure is shown in
 the scheme. The compound is a dimer of the starting
 material. The structure is shown in the scheme.

Robert E. Meyer
Anstalt für Anorganische Chemie, Basel
Helv., 18, 461-473 (1935)

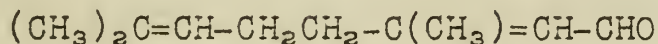
In a search for a method of synthesizing citral and similar naturally-occurring α , β -unsaturated aldehydes, the author investigated the following possibility:



The possibility of 1,4-addition of the Grignard to the hydroxymethylene ketone was also considered, in which case such a series of reactions would not lead to the desired products, but an α , β -unsaturated ketone.



Most of the work was carried out with 2-methyl-hepten-2-one-6 as the starting ketone and CH_3MgI as the Grignard, since the desired reactions would then lead to a known compound, citral.



The author was unable to obtain the hydroxycarbonyl compound in a pure form or any crystalline derivative. The crude product gave aldehyde tests with Schiff's and Tollen's reagents and on heating formed acetaldehyde and the original methyl heptenone. Dehydration resulted in an unsaturated compound, $\text{C}_{10}\text{H}_{16}\text{O}$, which was not citral but gave aldehyde tests with the above reagents. Permanganate oxidation of the partially reduced compound, $\text{C}_{10}\text{H}_{18}\text{O}$, obtained by starting with methyl heptanone, gave methyl caproic acid. This indicated $(\text{CH}_3)_2\text{C}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CO}-\text{CH}=\text{CH}-\text{CH}_3$ as the formula of $\text{C}_{10}\text{H}_{16}\text{O}$.

In an attempt to account for the formation of acetaldehyde and methyl heptenone, a study was made of the hydrolytic cleavage of double bonds which are conjugated with carbonyls. These cleavage products were formed from the hydroxycarbonyl compound both on heating and on treatment with 10 per cent K_2CO_3 solution. It was found that the α , β -unsaturated ketone also formed these products on alkaline hydrolysis.

The final proof of 1,4-addition of the Grignard was the fact that alkaline hydrolysis of the hydroxycarbonyl compound

Volume 11, No. 1
January 1, 1918
Chicago, Ill.
Published by the American Medical Association, 535 North Dearborn Street, Chicago, Ill.

In the year 1917, the American Medical Association published a special issue of the Journal of the American Medical Association, devoted to the subject of "The Medical Profession and the Public." This issue was published in the month of December, 1917, and was the first of a series of special issues to be published by the Association.

Table of Contents

Editorial: The Medical Profession and the Public, 1

Editorial: The Medical Profession and the Public, 1

The following is a list of the articles published in this issue of the Journal of the American Medical Association. The articles are arranged in alphabetical order of the authors' names. The names of the authors are given in full, and the titles of the articles are given in full. The titles of the articles are given in full, and the names of the authors are given in full.

Editorial: The Medical Profession and the Public, 1

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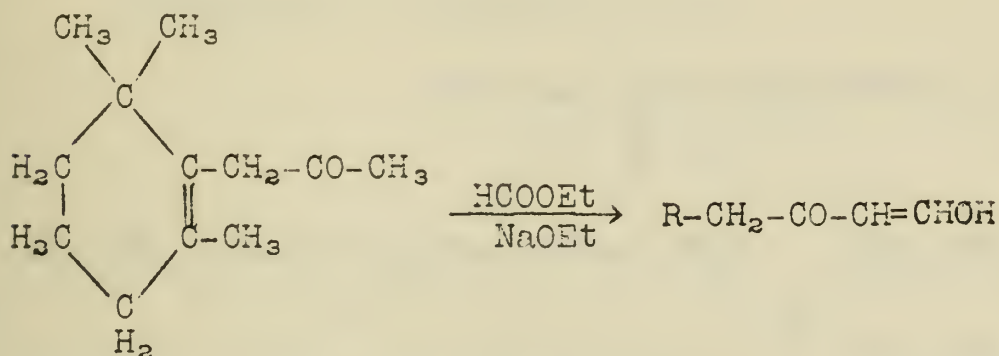
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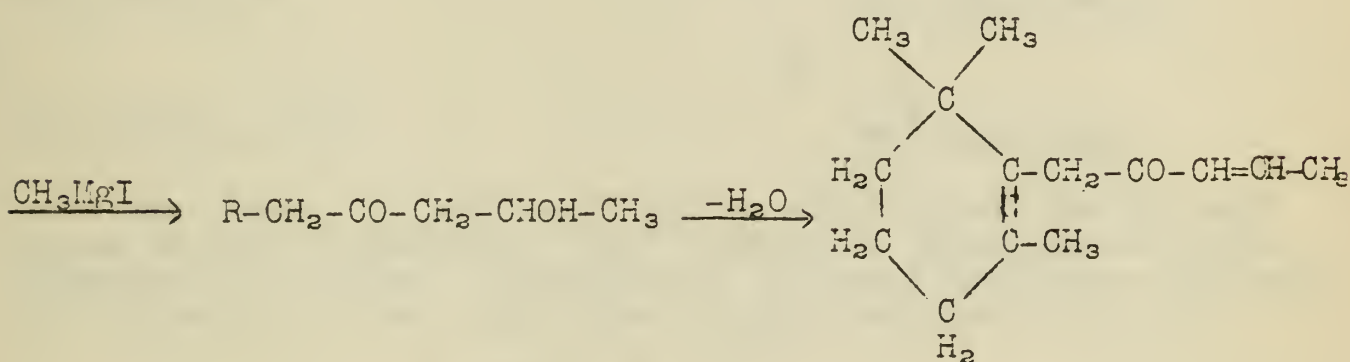
-2-

formed by the action of C_2H_5MgBr on hydroxymethylene methyl heptanone resulted in the formation of methyl heptanone with no trace of a higher ketone.

The synthesis of α , β -unsaturated aldehydes was thus shown to be impossible by the method investigated. This method was nevertheless found useful in the synthesis of an isomer of irone:



Cyclogeranyl-methyl-ketone



2',6',6'-trimethylcyclohexene-1-yl-1-pentene-3-one-2

Reported by P. S. Pinkney
November 25, 1935.

Existence of a β -Epoxy Tautomerism in
the Degradation Reactions of Certain Organic Compounds

38

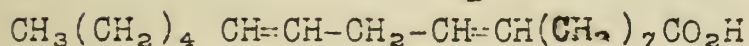
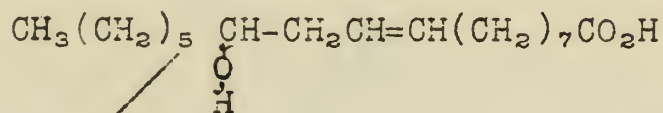
A. Barbot

Bull. Soc. Chim., 2, 895 (1935)

Bull. Soc. Chim., 2, 1438 (1935)

Institut de Chimie de Paris

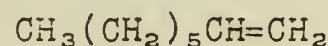
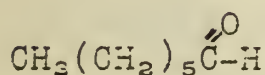
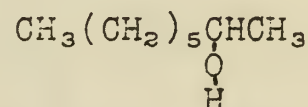
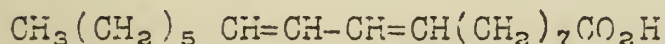
Reactions of ricinoleic acid:



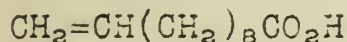
A.

+

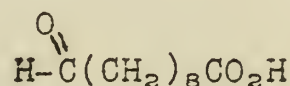
B.



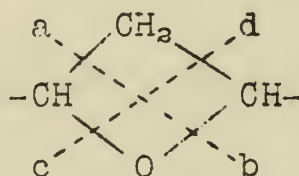
C.



D.



The theory is proposed that by addition of the hydroxyl group to the neighboring $\text{C}=\text{C}$ linkage a trimethylene oxide structure is formed. Reactions B, C, and D are then explained by a fission of the ring either along the line ab or cd.



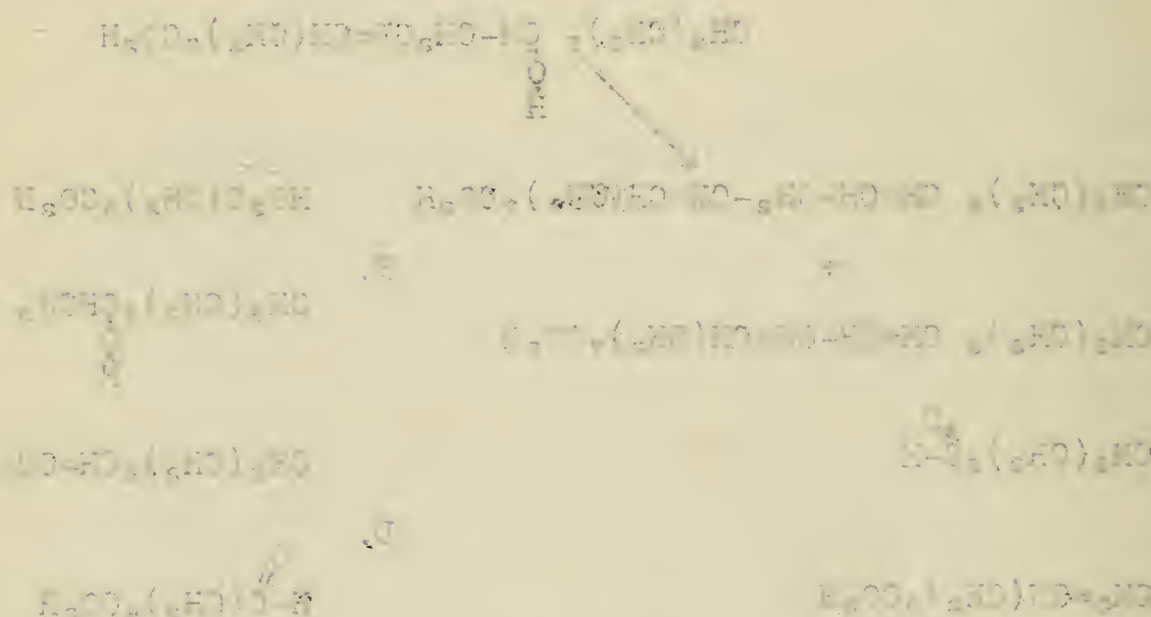
Evidence is offered for the plausibility of the assumption that this ring is formed.

A similar mechanism will explain a large number of other degradations, the requisite functional groups being a hydroxyl group, alcoholic, enolic, or acidic, and an unsaturated linkage between the gamma and delta atoms.

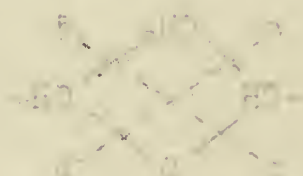
A. J. E. Robertson
 M.B. 1931, M.A. 1932, D. Sc. 1933
 M.B. 1934, M.A. 1935, D. Sc. 1936

Institute of Chemistry, University of London

Reaction of aldehydes with

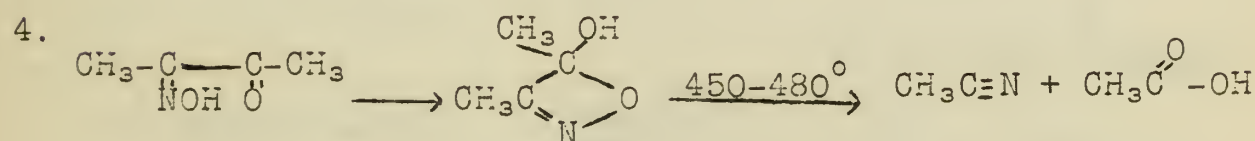
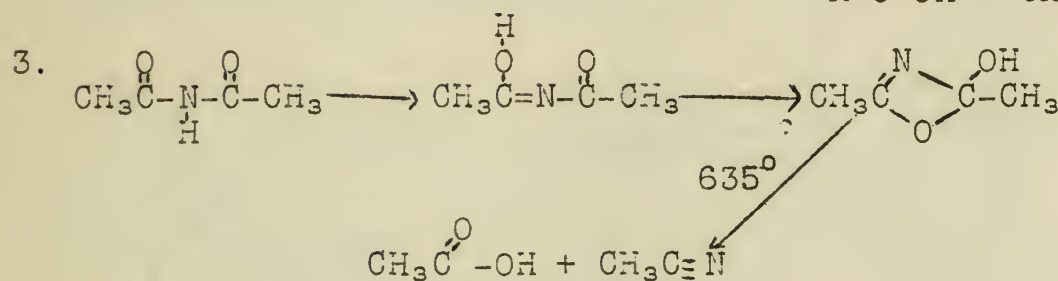
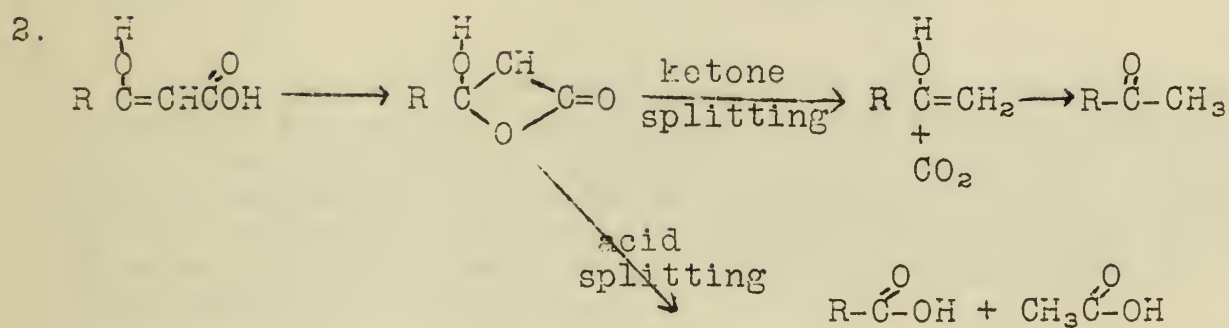
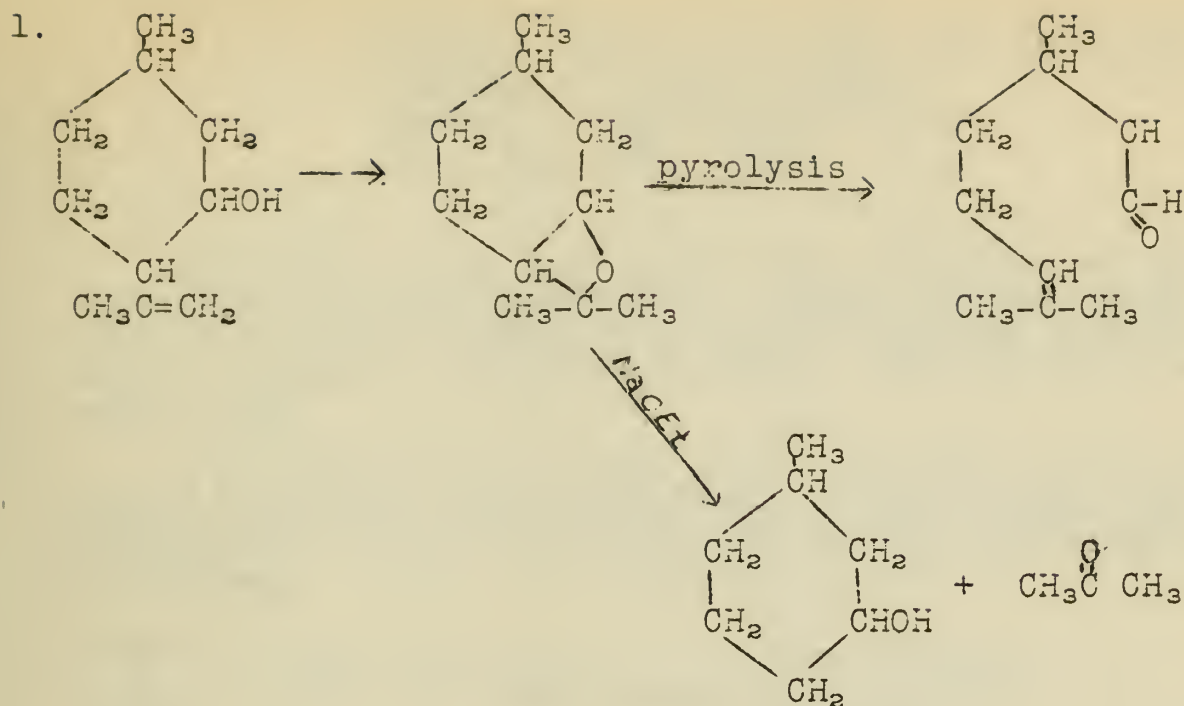


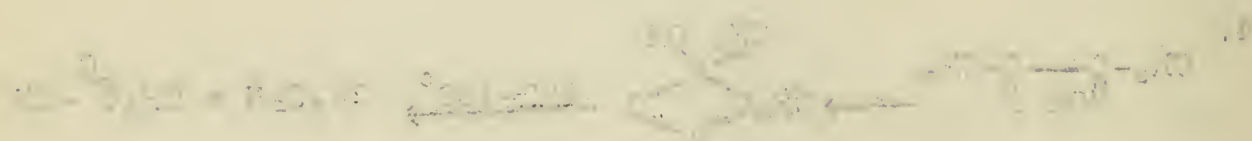
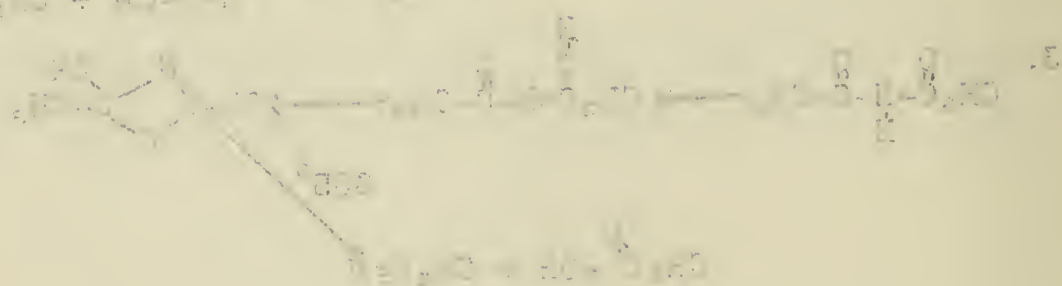
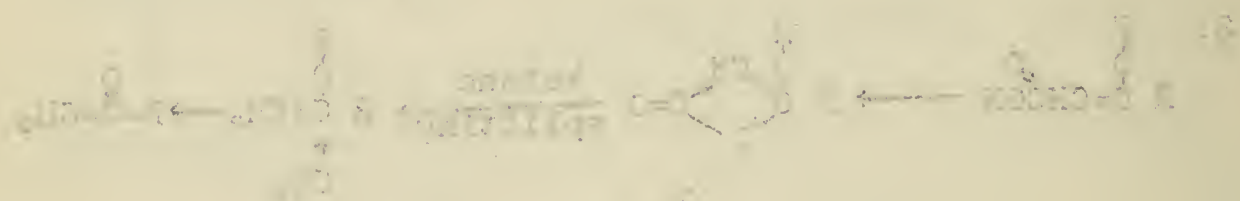
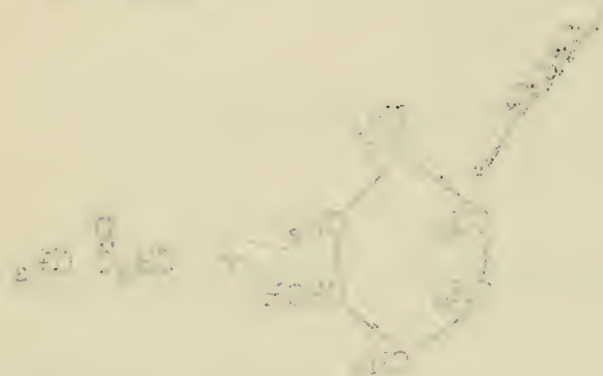
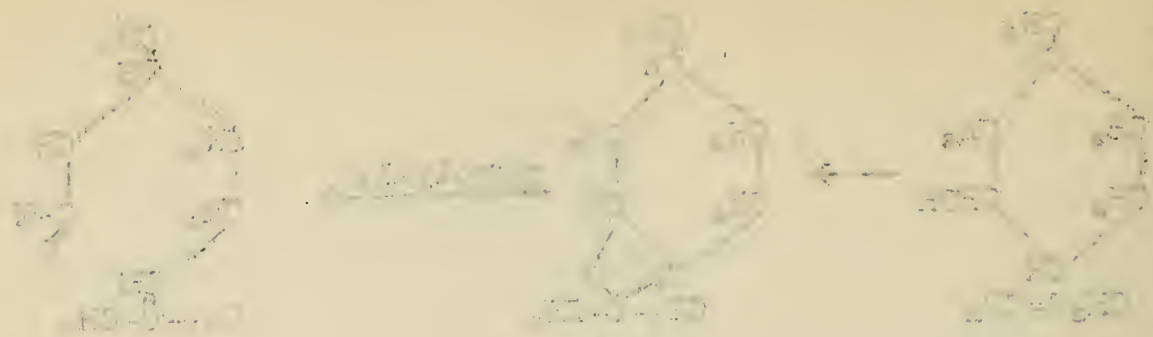
The theory is advanced that the addition of the hydroxyl group to the carbonyl group is a bimolecular reaction, involving the formation of a tetrahedral intermediate, which is then converted to the final product by a reaction of the type $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$.



Reference is made to the possibility of the formation of a tetrahedral intermediate, which is then converted to the final product by a reaction of the type $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$.

A similar reaction will occur with a carbonyl compound of the type $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$, and the reaction will be of the type $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$.

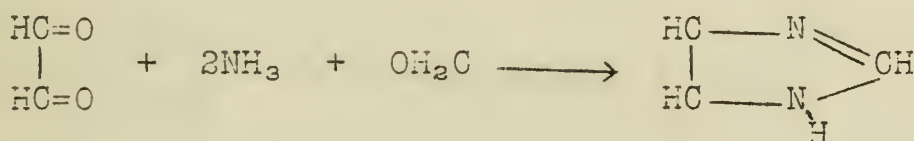




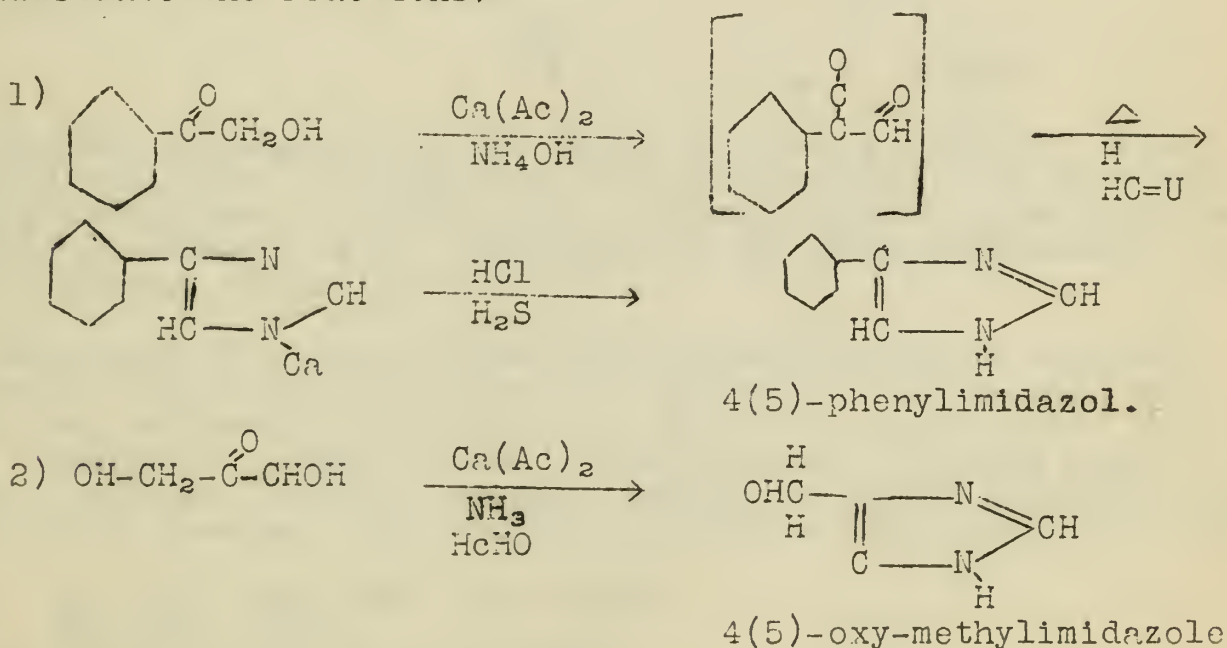
Weidenhagen and Herrmann.
 Biochem. Abteil. d. Instituts für Zucker -
 Industrie, Landwirtschafte.
 Abteil. d. Universität Berlin.
 Ber., 68, 1953 (1935)

For a long time biochemists have attempted to synthesize imidazoles in large quantities. During the past fifty years several synthetic methods have been developed, but none of them is a simple and smooth reaction. The yield in every case is low.

A new synthesis of imidazoles was worked out by the authors based on the previous work of Radziszewski who synthesized imidazol from glyoxal, ammonia and formaldehyde as follows:



The limitation of this method is that diketones are difficult to obtain. The authors found that 1,2-oxyketone or 1,2-oxyaldehyde, in the presence of ammoniacal cupric acetate solution, is oxidized immediately to the 1,2-diketone. In the presence of aromatic or aliphatic aldehyde, the ring closure proceeds immediately. The following examples will illustrate the reactions.--



Fifteen substituted imidazols were prepared. Most of the reactions are smooth and some of the yields are as high as ninety per cent.

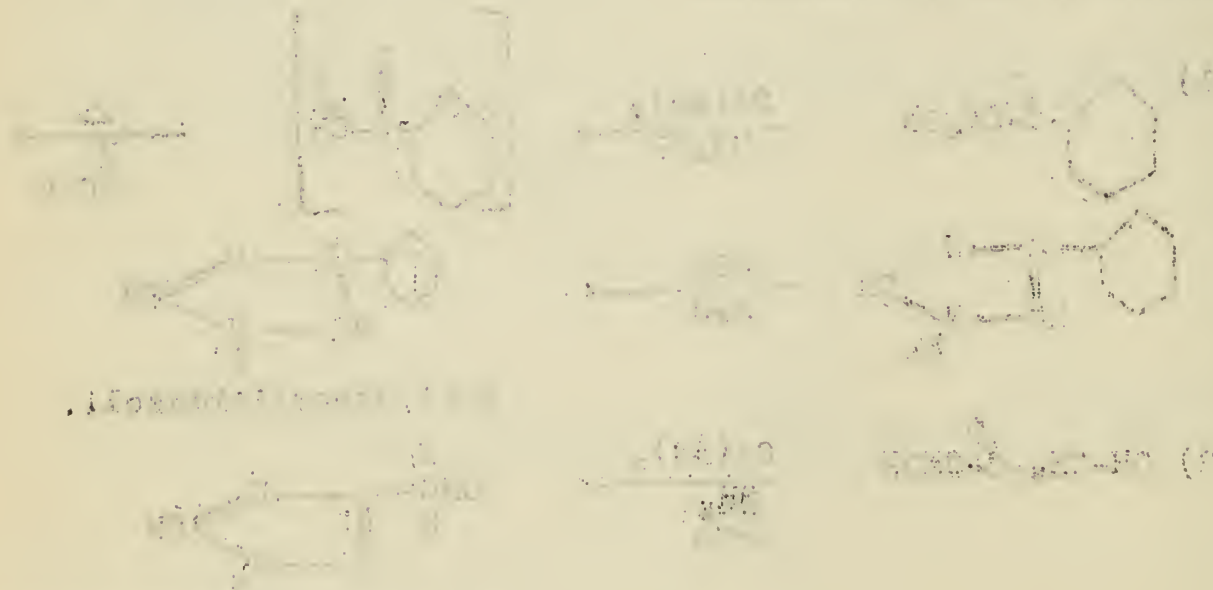
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A new feature of the Journal is the "Medical News" section, which contains the latest news from the medical world. It is published for the Association by the American Medical Association, 535 North Dearborn Street, Chicago, Ill. 60610.



The reaction of nitrobenzene with sulfuric acid is a well-known reaction. It is published for the Association by the American Medical Association, 535 North Dearborn Street, Chicago, Ill. 60610.

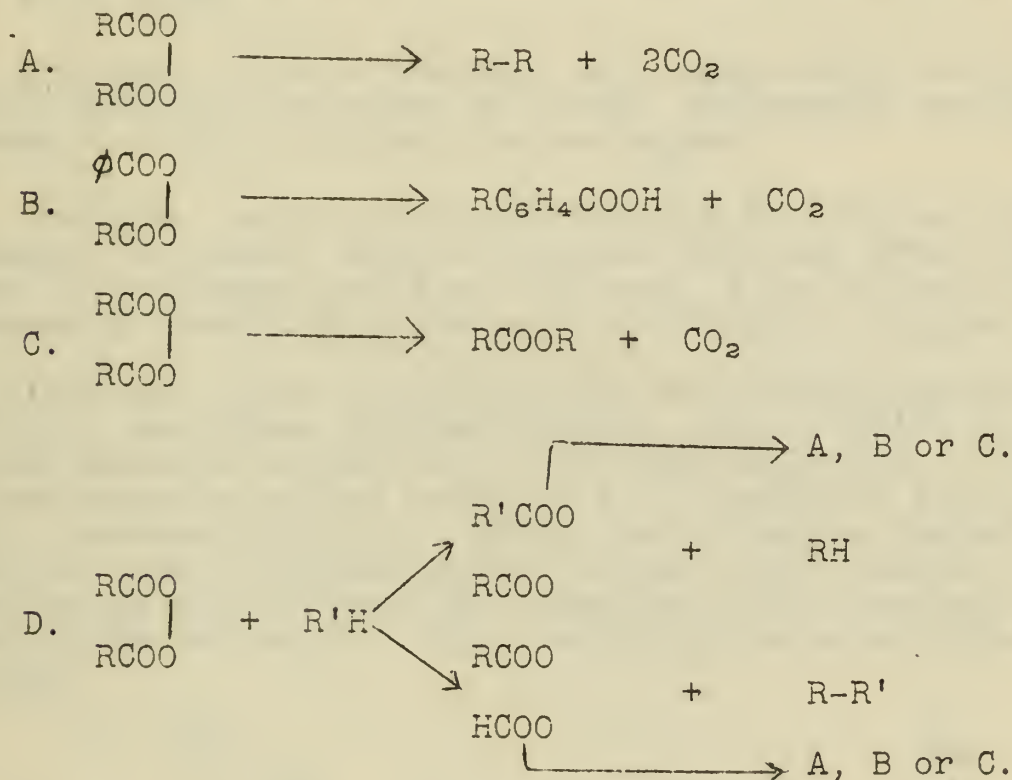


The reaction of nitrobenzene with sulfuric acid is a well-known reaction. It is published for the Association by the American Medical Association, 535 North Dearborn Street, Chicago, Ill. 60610.

P. H. Hermans, Rec. trav. chim., 54, 760 (1935)
Breda Laborat. der Hollandische Kunstzyde Industrie.
Previous work: Acylperoxides.

A new scheme to explain the various reactions of diacylperoxides is formulated by the author, replacing an older one advanced in 1926.

Diacylperoxides can react in any of the following ways:



Thermal decomposition can cause reaction A, B or C. Ali-phatic peroxides react preferentially according to A when thermally decomposed. Aromatic and aromatic-aliphatic peroxides can react according to A or, depending on the particular nature of the R groups, according to B or C.

Reactions of acylperoxides with other substances follow D. There is a possibility of two new peroxides being formed which, in turn, can react according to A, B or C. The term R'H in D is not limited to a hydrocarbon. Reactions were studied where R'H was an alcohol, a base, an alkyl halide, a cyclic saturated hydrocarbon, benzene, substituted benzenes and an aliphatic acid.

Ber., 58, 287, 476, 765, 770 (1925)
Ber., 59, 664 (1926)
J. Am. Chem. Soc., 27, 161 (1905)
Rec. trav. chim., 46, 72 (1927)
Rec. trav. chim., 48, 933 (1929)
Rec. trav. chim., 49, 102 (1930)
Ann., 513, 105 (1934)

Reported by W. E. Ross
December 4, 1935

The Structure of Oestrin, Equilin and Equilenin

A. Cohen, J. W. Cook, C. L. Hewett

Research Institute of The Cancer Hospital (Free), London
J. Chem. Soc., 1935, 445

Previous work:

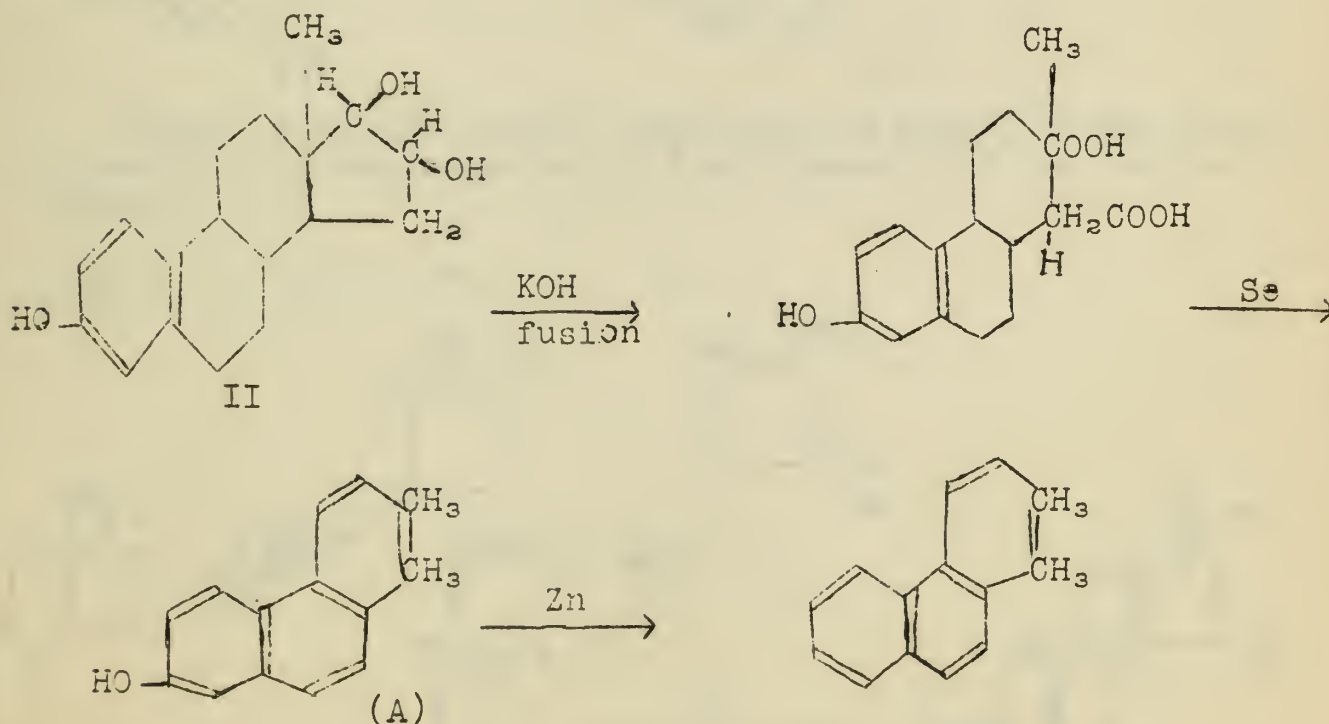
Cook and Hewett - polycyclic aromatic hydrocarbons, carcinogenic substances, substances related to sterols and bile acids.

Cohen - synthesis of substances related to sterols and bile acids.

Oestrone (I) and oestriol (II) were first isolated from gravid urine of the human by Doisy,¹ Butenandt² and Marrian.³ A number of other sources are now known.

Oestrone (also called theelin and follicular hormone), $C_{18}H_{22}O_2$, is weakly acidic, has one phenolic group, adds six atoms of hydrogen, melts at 250° and is dextro-rotatory. Clemmensen reduction produces desoxotheelin, $C_{18}H_{24}O$.

Oestriol (also called theelol and trihydroxyoestrin), $C_{18}H_{24}O_3$, has three hydroxyl groups, one of which is acidic. It has phenolic properties, adds three molecules of hydrogen, is dextro-rotatory and melts at 273° . Oestriol distilled over $KHSO_4$ produces oestrone. Early investigation showed that oestriol fused with KOH gave a dibasic acid, which, by selenium dehydrogenation followed by reduction with zinc dust, gave 1,2-dimethylphenanthrene.⁴ The reactions are interpreted as indicated:



The final product is identical to 1,2-dimethylphenanthrene synthesized from naphthalene and partially synthesized from aetiobilianic acid (a degradation product of cholanic acid). 7-Hydroxy-1,2-dimethylphenanthrene synthesized by Haworth⁵ was identical to the substance (A) above.

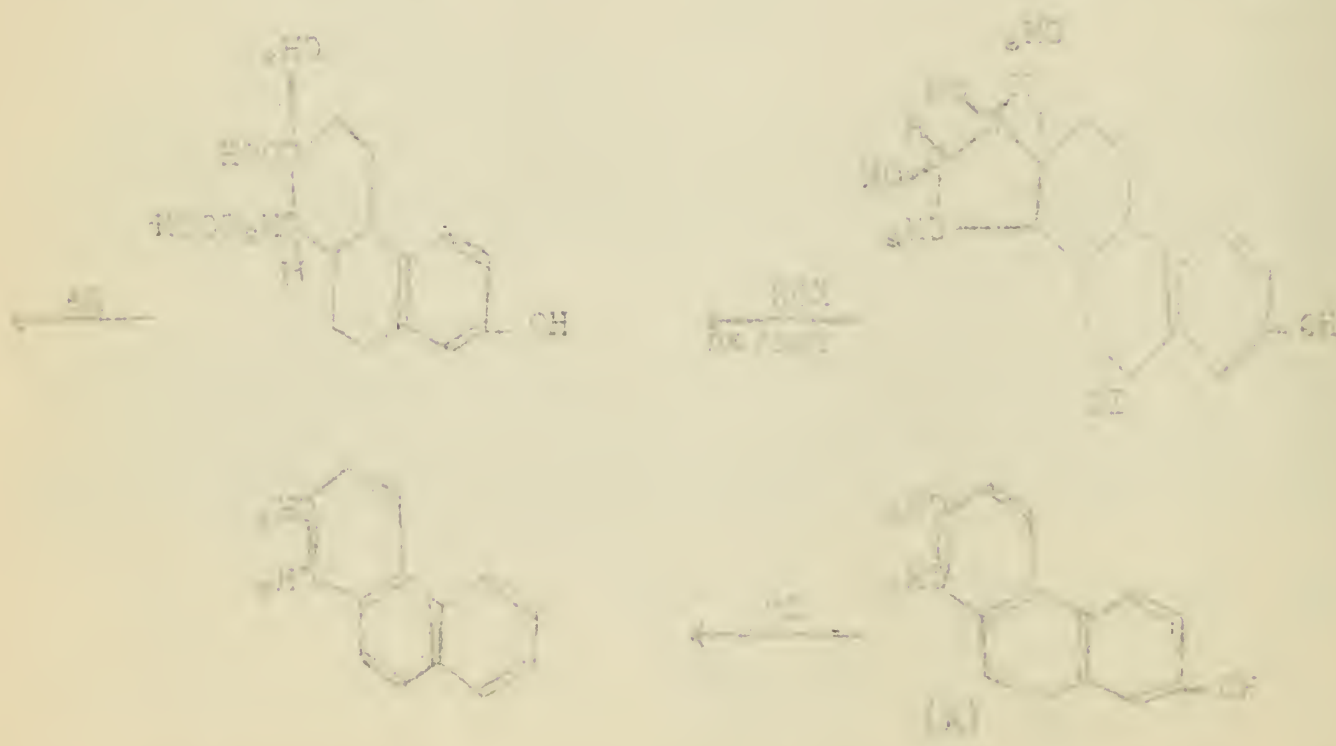
A. Collins, J. W. Smith, & J. E. Hester
 Research Institute of the Central Research (Chemical) Division
 U. S. Army, Dept. of Defense, Washington, D. C.

Several new compounds have been prepared and their properties are being investigated. These compounds are of interest in the study of the chemistry of the indole nucleus. The following are the names of the compounds and their properties:

Compound (I) and compound (II) were found to be isomers of the same molecular formula, $C_{12}H_{11}N$. Compound (I) is a solid, m.p. 100°C, and compound (II) is a liquid, b.p. 100°C.

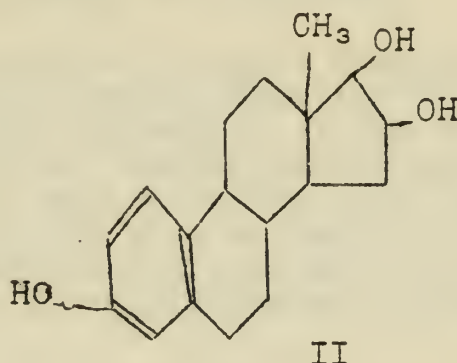
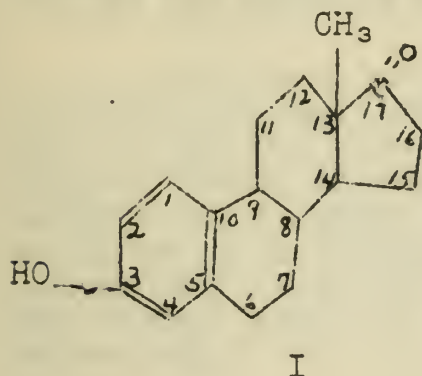
Compound (I) is a solid, m.p. 100°C, and compound (II) is a liquid, b.p. 100°C. Both compounds are soluble in benzene, chloroform, and carbon tetrachloride. They are also soluble in concentrated sulfuric acid.

Compound (I) is a solid, m.p. 100°C, and compound (II) is a liquid, b.p. 100°C. Both compounds are soluble in benzene, chloroform, and carbon tetrachloride. They are also soluble in concentrated sulfuric acid. The following are the chemical structures of compounds (I) and (II):

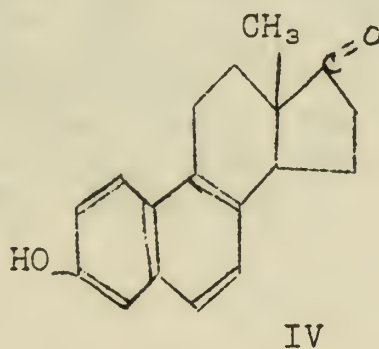
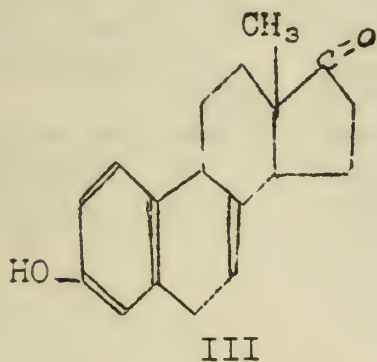


The final product is a solid, m.p. 100°C, and is soluble in benzene, chloroform, and carbon tetrachloride. It is also soluble in concentrated sulfuric acid. The following are the chemical structures of the final product and its reaction scheme:

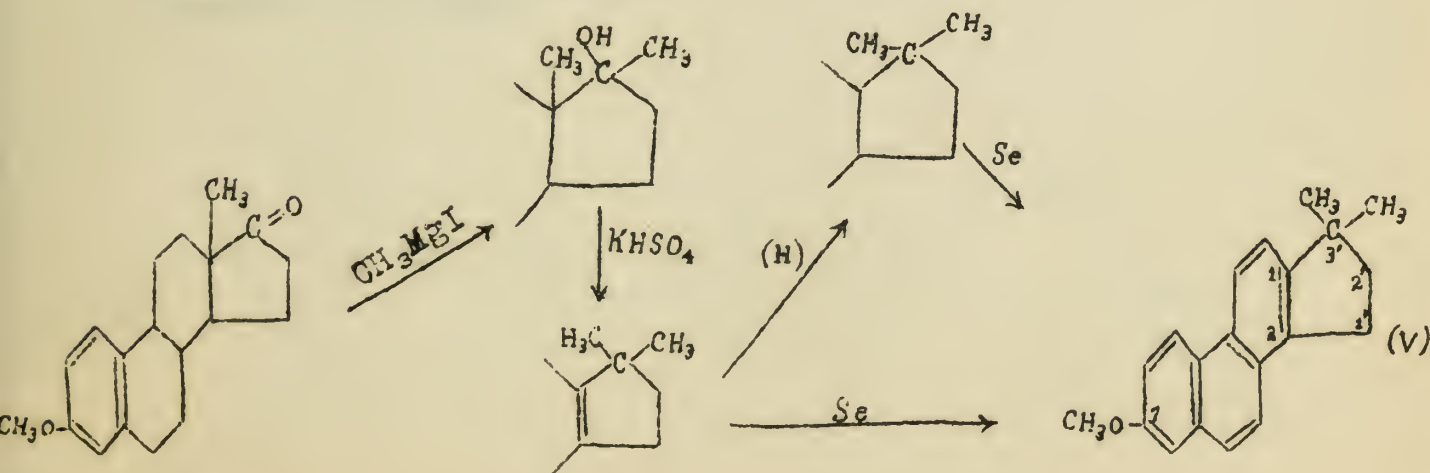
From these facts and others the following structures have been assigned to oestrone (I) and oestriol (II), the positions of the methyl group, the keto group and the two non-phenolic hydroxyls alone remained to be definitely proved by the present work of Cohen, Cook and Hewett:



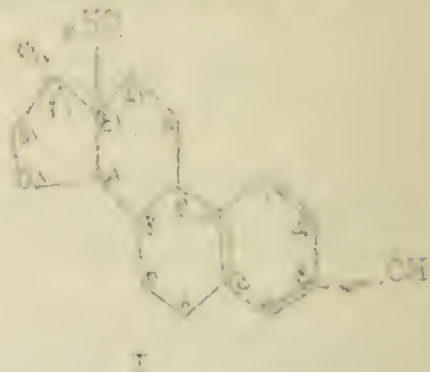
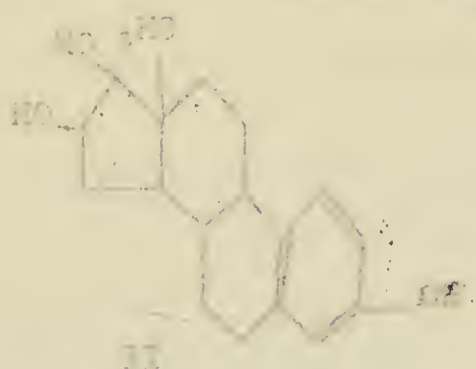
Equilin, $C_{18}H_{20}O_2$, and equilenin, $C_{18}H_{18}O_2$, were first obtained from the urine of mares by Girard.⁶ The structure assigned to equilin is (III),⁷ and to equilenin (IV):



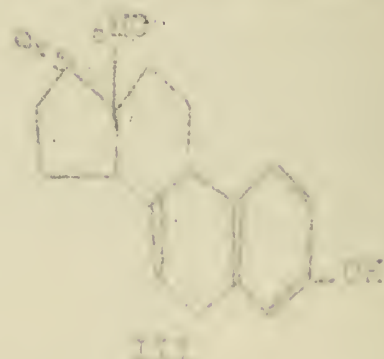
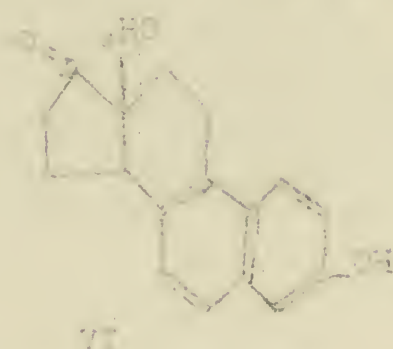
Cohen, Cook and Hewett completed the proof of the structures I-IV by reactions which they showed to occur as indicated:



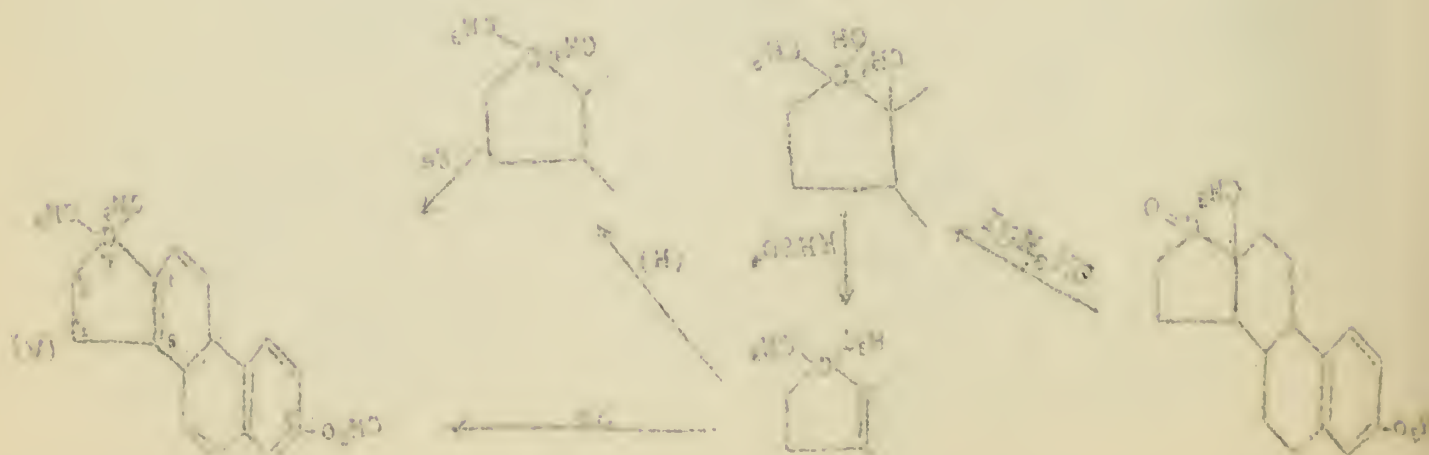
From these facts and from the following observations have been assigned to structure (I) and (II) the positions of the hydroxyl groups, the first group and the second group. Hydroxyl groups are assigned to be 1-hydroxyl and 2-hydroxyl as shown in the following work of Brown, Cook and Hewitt:



Reaction of $\text{C}_{21}\text{H}_{34}\text{O}_2$ and $\text{C}_{21}\text{H}_{34}\text{O}_3$ with H_2 over $\text{Pt}/\text{H}_2\text{SO}_4$ gave $\text{C}_{21}\text{H}_{36}\text{O}_2$ and $\text{C}_{21}\text{H}_{36}\text{O}_3$ respectively. The structure assigned to $\text{C}_{21}\text{H}_{36}\text{O}_2$ is (III), and to $\text{C}_{21}\text{H}_{36}\text{O}_3$ is (IV):



Brown, Cook and Hewitt completed the proof of the structure of I-IV by reactions which they showed to occur in the following sequence:



The methyl ether of each of I, III and IV was used as starting material, each substance giving the same final product. The investigators expected the product to be either the 1', 2' or 3'-methyl derivative of 7-methoxy-1,2-cyclopentenophenanthrene. Each of these substances are synthesized, but did not correspond to their end-product. V was synthesized and found to be identical to the product of their series of reactions.

The reactions are considered to give indisputable evidence of position 13 for the methyl group in the hormones and 17 for the keto group. The migration of the methyl group occurs during dehydration and not during dehydrogenation. The authors have shown, however,⁷ that when the keto group or oestrone or equilenin was reduced to a methylene group and the methyl ether of the product dehydrogenated by selenium, the methyl group at position 13 is eliminated instead of migrating.

1. Doisy, et al, J. Biol. Chem., 86, 499 (1930); 91, 641 (1931).
2. Butenandt, Z. physiol. Chem., 191, 127 (1930); 199, 243 (1933).
3. Marrian, Biol. Chem. J., 24, 435 (1930); 26, 27 (1932).
4. Chem. Ind., 52, 268 (1933).
5. Haworth and Sheldrick, J. Chem. Soc., 1934, 864.
6. Girard, et al, Compt. rend., 194, 909; 194, 1020 (1932).
7. Cohen, et al, J. Chem. Soc., 1934, 653.

Reported by Allene Jeanes
December 11, 1935.

The methyl ether of each of I, III and IV was used as starting material, each substance giving the same final product. The investigation supported the previous conclusion that the 3'-methyl derivative of 2-methoxy-1,2-cyclohexanediol is not a derivative of these which was not isolated, but did not correspond to their composition. It was synthesized and found to be identical to the product of their series of reactions.

The reactions are considered to give indistinguishable evidence of position II for the methyl group in the homomeric and IV for the keto group. The migration of the methyl group occurs during dehydration and not during dehydration. The authors have shown, however, that when the keto group is destroyed by oxidation was reduced to a methylene group and the methyl ether of the product was hydrolyzed by sodium, the methyl group at position II is eliminated instead of migrating.

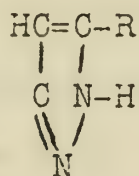
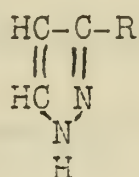
1. Doherty, et al., J. Biol. Chem., 58, 422 (1933); 51, 641 (1931); 51, 641 (1931).
2. Gutierrez, E. J. Biol. Chem., 131, 127 (1936); 132, 242 (1937).
3. Harrison, E. J. Biol. Chem., 131, 127 (1936); 132, 242 (1937).
4. Chem. Ind., 22, 208 (1933).
5. Haworth and E. J. Biol. Chem., 131, 127 (1936); 132, 242 (1937).
6. Haworth, et al., J. Biol. Chem., 131, 127 (1936); 132, 242 (1937).
7. Cohen, et al., J. Biol. Chem., 131, 127 (1936); 132, 242 (1937).

Reported by Alfred Cohen
December 11, 1937.

v. Auwer und Breyhan
Jour. für Prakt. Chemie (2), 143, 259, (1935)

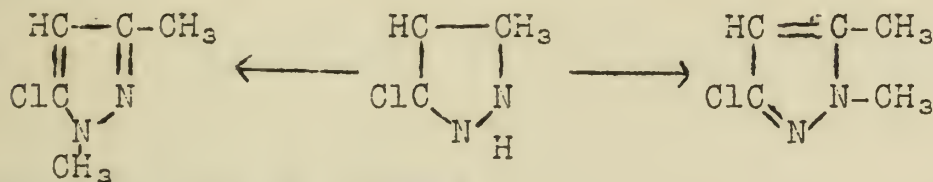
This paper is the latest of a series by v. Auwers and co-workers dealing with the substitution of pyrazoles and the problem of isomers formed from such substitution. Acylation and alkylation results are presented.

A C-substituted pyrazole as $\text{HC}-\text{C}-\text{R}$ when further N-substituted may give rise to isomers. This is due to the possibility of the structure of the compound represented, isomerising into



There is probably a dynamic equilibrium between these formulas but when further substitution occurs isomers are formed.

Various alkylation and acylation reagents and conditions have been used but no generalizations have been made. For example:

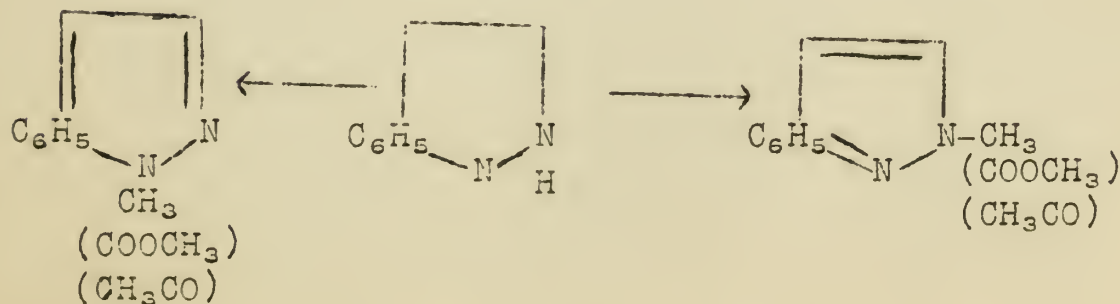


chief product $\longleftarrow (\text{CH}_3)_2\text{SO}_4 + \text{alkali}$

100 per cent $\longleftarrow \text{CH}_3\text{Br}$

chief product $\longleftarrow \text{CH}_2\text{N}_2$

$\text{Na salt} + \text{CH}_3\text{I} \longrightarrow 100\%$



$\text{CH}_3\text{Br} \longrightarrow$ chief product

100 per cent $\longleftarrow \text{Na salt} + \text{CH}_3\text{I}$

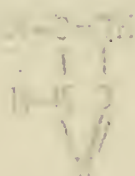
$\text{ClCOOCH}_3 \longrightarrow$ only.

only $\longleftarrow \text{CH}_3\text{COCl}$

Wittig Reaction in the Synthesis of
Alkenes and Alkynes

This paper is the first of a series of papers by J. Wittig and
Wittig Reaction in the Synthesis of Alkenes and Alkynes
Wittig Reaction in the Synthesis of Alkenes and Alkynes

A Wittig reaction of aldehyde with
Wittig Reaction in the Synthesis of Alkenes and Alkynes
Wittig Reaction in the Synthesis of Alkenes and Alkynes



There is probably a dynamic
Wittig Reaction in the Synthesis of Alkenes and Alkynes
Wittig Reaction in the Synthesis of Alkenes and Alkynes

Various Wittig reactions and Wittig Reaction in the Synthesis of Alkenes and Alkynes
Wittig Reaction in the Synthesis of Alkenes and Alkynes



Wittig Reaction in the Synthesis of Alkenes and Alkynes

Wittig Reaction in the Synthesis of Alkenes and Alkynes

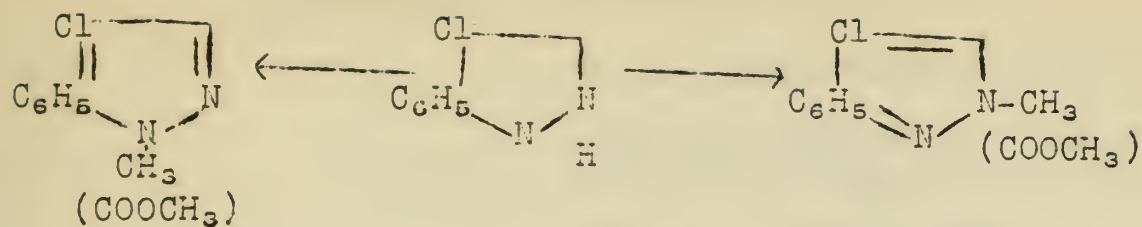
Wittig Reaction in the Synthesis of Alkenes and Alkynes

Wittig Reaction in the Synthesis of Alkenes and Alkynes



Wittig Reaction in the Synthesis of Alkenes and Alkynes

Wittig Reaction in the Synthesis of Alkenes and Alkynes



$\text{CH}_3\text{Br} \longrightarrow$ chief product.

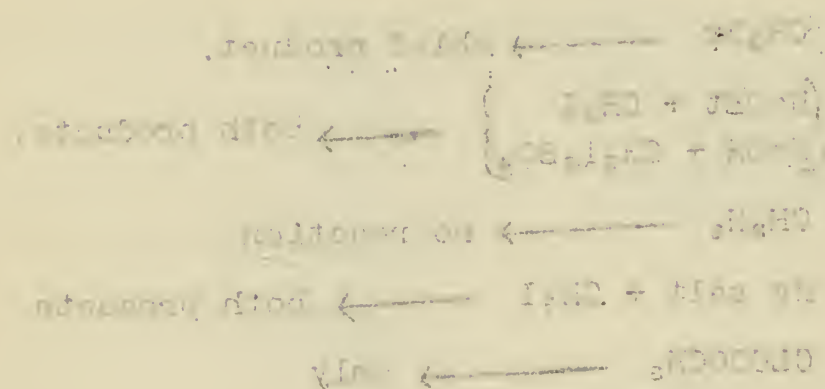
$\left\{ \begin{array}{l} \text{NaOEt} + \text{CH}_3\text{I} \\ \text{NaOH} + \text{CH}_3\text{I}_2\text{SO}_4 \end{array} \right\} \longrightarrow$ both products.

$\text{CH}_2\text{N}_2 \longrightarrow$ no reaction

$\text{Na salt} + \text{CH}_3\text{I} \longrightarrow$ both products

$\text{CLCOOCH}_3 \longrightarrow$ only

Reported by G. E. Ulliot
December 11, 1935



Reported by G. E. Elmer
 December 13, 1943

Condensation of 3-methyl-buten-2-al-1.

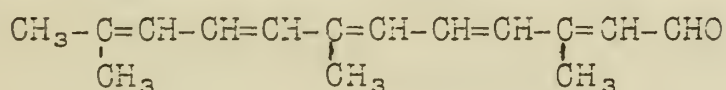
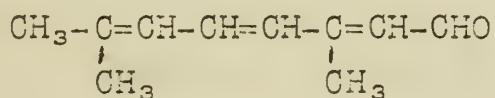
F. G. Fischer and Coworkers.

From the Chemical Laboratories
of the Freiberg UniversityBer., 68, 1726 (1935)Ber., 64, 30 (1931)Ann., 494, 263 (1932)

The synthesis of carotinoid chains, such as occur in Vitamin A, Carotin, Crocetin, and other naturally-occurring products, is now possible although none of these products has as yet been prepared.

Karrer, Ruzicka, and Gould and Thompson have synthesized hydrogenated carotincid chains, while Kuhn and others have built up several series of conjugated unsaturated carbon chains.

Fischer has been able to condense β -methyl-crotonaldehyde with itself to give the following:



These have also been reduced to the corresponding alcohols.

Reported by Wm. E. Lundquist

December 13, 1935.

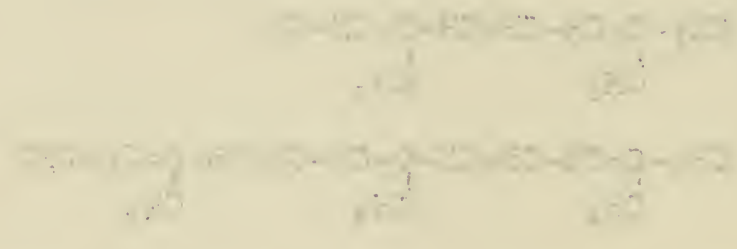
J. H. Van Vleet and J. H. Van Vleet

Department of Chemistry, University of California, Berkeley, California

(Received July 11, 1932)
(Published August 1, 1932)

The spectrum of the hydrogen atom, as observed in the laboratory, is not a simple one. It is a complex of many lines, each of which is a result of a different transition. The lines are not equally spaced, and their intensities are not equal. The spectrum is a result of the interaction of the electron and the proton, and it is a result of the quantization of the energy levels. The spectrum is a result of the quantization of the energy levels, and it is a result of the interaction of the electron and the proton.

It is well known that the spectrum of the hydrogen atom is a result of the quantization of the energy levels. It is well known that the spectrum of the hydrogen atom is a result of the quantization of the energy levels.



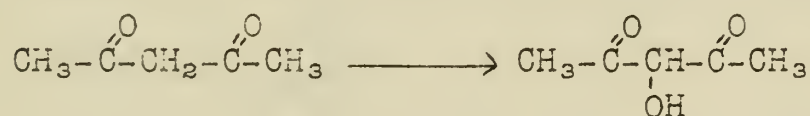
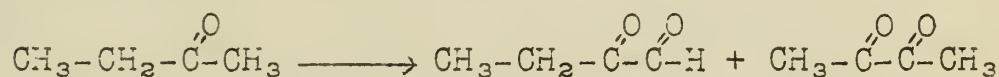
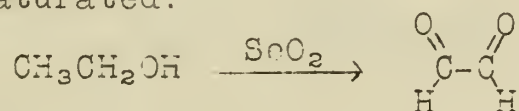
These lines are also known as the Balmer series.

Postowsky, J. J., Ber., 68B, 852-6 (1935)
 Henze, M., Ber., 67B, 752-3 (1934)
 Schwenk-Borquero, Ber., 65, 1601 (1932)
 Union, Edmond, Compt. Rend., 199, 363-5 (1934)
 Truchet, M. M., Compt. Rend., 196, 706-9 (1933)
 Dupont, G., Bull. Soc. Chem., 53, 599-603 (1933)
 Riley, H. L., J. Chem. Soc., 1934, 844-8
 Riley, H. L., J. Chem. Soc., 1935, 901-4
 Riley, H. L., J. Chem. Soc., 1932, 2342-4

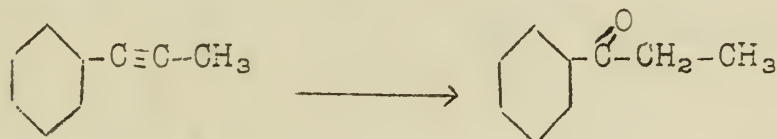
Selenium dioxide has become one of the best-known specific oxidizing agents available. In many cases by a single oxidizing reaction using selenium dioxide, it is possible to obtain in good yields compounds which are difficult to obtain by standard synthetic methods.

I. Aliphatic Series

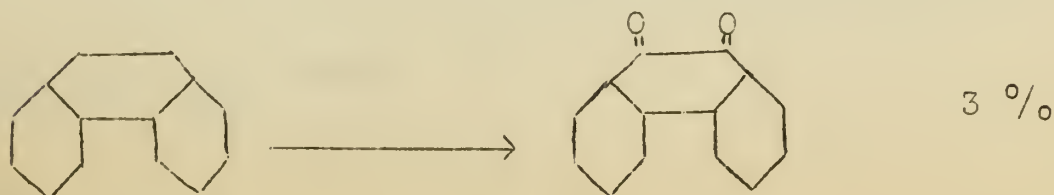
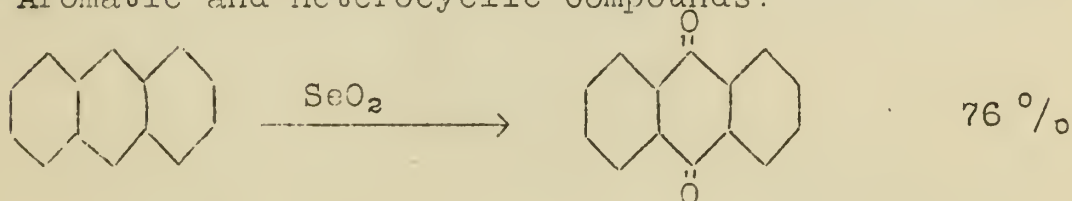
a) Saturated.



b) Unsaturated.



II. Aromatic and Heterocyclic Compounds.



(15089) 2-10-1914
 (15090) 2-10-1914
 (15091) 2-10-1914
 (15092) 2-10-1914
 (15093) 2-10-1914
 (15094) 2-10-1914
 (15095) 2-10-1914
 (15096) 2-10-1914
 (15097) 2-10-1914
 (15098) 2-10-1914
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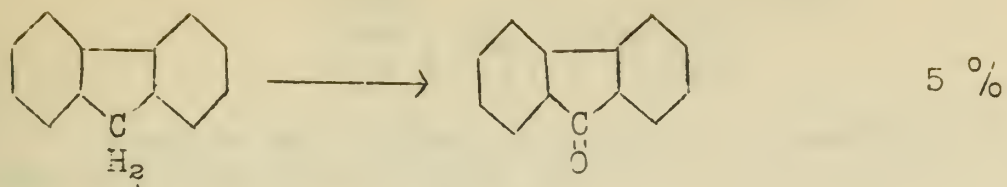
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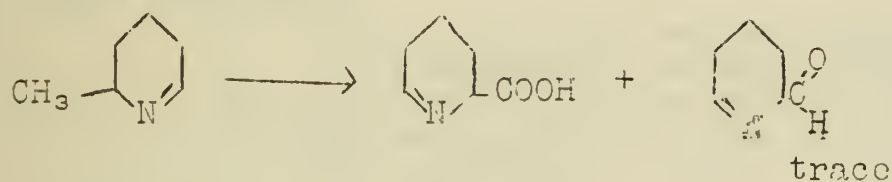
15089-15099



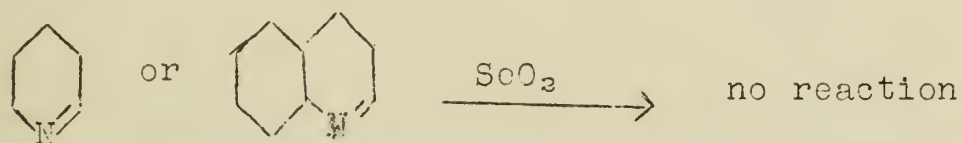
5 %



trace

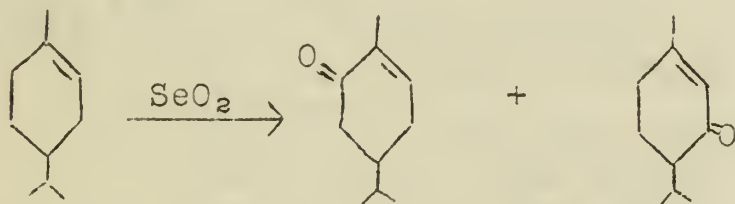
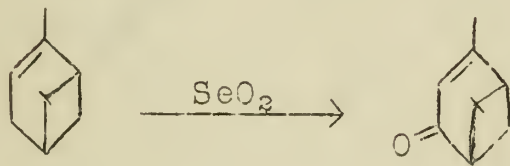


trace

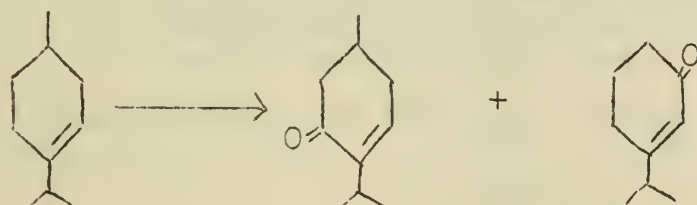


no reaction

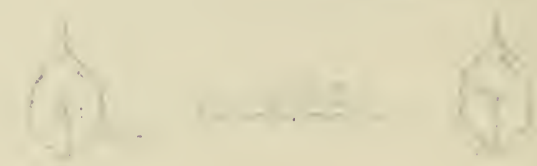
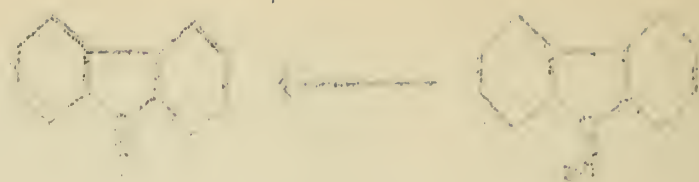
III. Terpenes



none of this

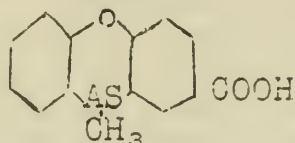


none of this



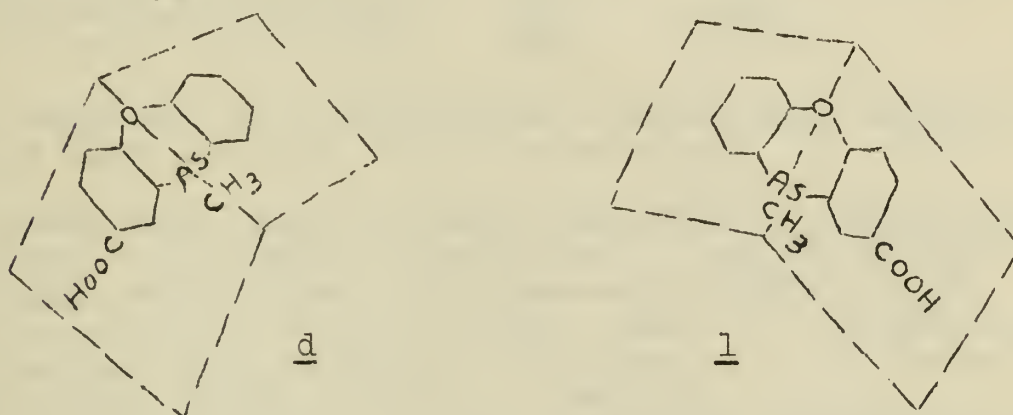
Kamai, Lesslie and Turner
 Ber., 68, 1893 (1935)
 J.C.S., 1170 (1934)

Lesslie and Turner succeeded in resolving 10-methyl-phenoxarsine-2-carboxylic acid.



Two possible sources of optical activity in this compound were postulated.

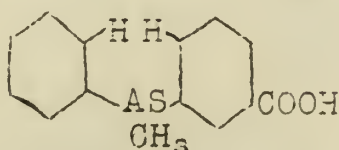
1. The activity may be due entirely to the presence of an asymmetric arsenic atom.
2. The activity may be due to asymmetry of the molecule which results from a folded structure, as below.



The folded structure is accepted as being the cause of the activity for the following reasons;

1. The atomic radii of arsenic and oxygen are widely different.
2. Calculations from the valence angles of the two atoms indicate that greater stability would result from a folded rather than a planar structure.
3. No known arsines have, as yet, been resolved.
4. Racemization, caused by addition of ethyl iodide, can be easily explained.

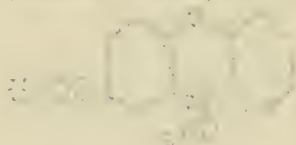
Kamai synthesized the o, m, and p isomers of the following compound.



Inability to resolve any of these compounds is given as further evidence in favor of the folded structure of 10-methyl-phenoxarsine-2-carboxylic acid.

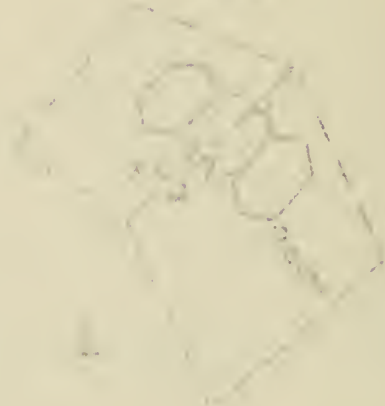
Final, 4/1/1954
1000
1000
1000

Isolate and then subjected to further investigation
Phenanthrene-2-carboxylic acid



The following results of optical activity in this compound were obtained:

1. The optical activity of the compound in the presence of 2% aqueous solution of sodium hydroxide.
2. The optical activity of the compound in the presence of 2% aqueous solution of sodium hydroxide.



The following results were obtained as shown in the table of the optical activity of the compound:

1. The optical activity of the compound in the presence of 2% aqueous solution of sodium hydroxide.
2. The optical activity of the compound in the presence of 2% aqueous solution of sodium hydroxide.

From the above results it is evident that the compound is optically active.



The following results were obtained as shown in the table of the optical activity of the compound:

- A. H. Blatt, J. Am. Chem. Soc., 57, 1103 (1935)
 F. Micheel and W. Schulte, Ann., 519, 70 (1935)
 P. Karrer and V. Segesser, Helv. Chim. Acta, 18,
 273 (1935)
 P. Karrer and C. Musante, Helv. Chim. Acta, 18,
 1140 (1935)

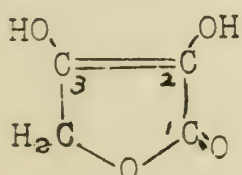
Karrer and V. Segesser have shown that the following formois of the general formula, $R-CO-CHOH-COCOR$, exist in equilibrium of the benzoin-ene-diol type. They have investigated this equilibrium quantitatively, by iodine titration, and give the following results:

		Per cent M.P. Ene-Diol Content	Per cent Carbonyl Content
Benzoylformoin		57	43
p-p-Dimethoxybenzoylformoin	151-2	40	60
p-p-Dichlorobenzoylformoin	190	100	--
p-p-Dibromobenzoylformoin	196	95-100	5-0

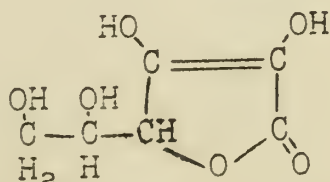
These compounds all reduce acetic acid-copper acetate solution, and are thus oxidized to the tetraketone.

Blatt has shown, through alkylation of benzoylformoin, two types of monomethyl derivatives. One of these is a glycosidic ether type of the general formula $R-C(=C(OH)-CO-C(OR')-R$. This is proven by convertibility, ease of formation, and blocking of the carbonyl group towards addition. The second type of derivative is the open-chain monomethyl ether of formula $R-C(=C(OH)-CO-C(OR)-R$. This derivative reacts with ortho-phenylenediamine to give a quinoxaline. It is obtained from the dimethyl derivative by removing the glycosidic alkyl group.

Micheel and Schulte compare the oxytetrone acid (I) and its alkylation derivatives to ascorbic acid (II) and its alkylation derivatives.



I.



II.

They are able to show that the C_3 -atom is the one holding the strongly acidic hydroxyl group. This is accomplished by the ozonization of the two isomeric monoalkyl ethers, which are formed by entirely different methods.

H. Staudinger, G. V. Schulz,
Ber., 68, 2313, (1935).

The report includes various types of molecular weight determinations used by Staudinger on high polymeric products.

The use and limitation of the following methods will be given:

1. Osmotic pressure method.
2. Viscosity method.
3. End group determination method.
4. Cryoscopic method.
5. Modification of above methods.

By use of a number of different methods in determining molecular weight of a polymer the limitations of a particular method were ascertained. Explanation for abnormal behavior was given in all these cases.

Reported by Rob't. Johnson

January 15, 1936.

Dr. G. V. Schulz
P.O. Box 11234

The present instrument is used for the determination of the molecular weight of polymers by the method of light scattering.

The use and limitations of the instrument are given

will be given:

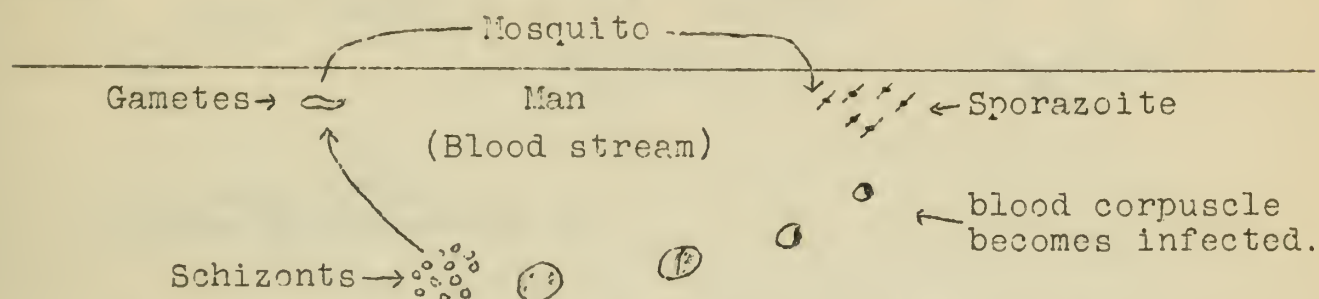
1. Optical pressure method.
2. Viscometry method.
3. End group determination method.
4. Cryoscopic method.
5. Limitation of above methods.

By use of a number of different methods in determining molecular weight of a polymer the limitations of a particular method are recognized. Comparison of abnormal behavior has given in all these cases.

Reported by Dr. G. V. Schulz

January 10, 1950.

Malaria exists in three forms, malaria tertian, quartan, and tropical. The life cycle of the malaria germs, mosquito-man-mosquito, is of fundamental importance. (1)

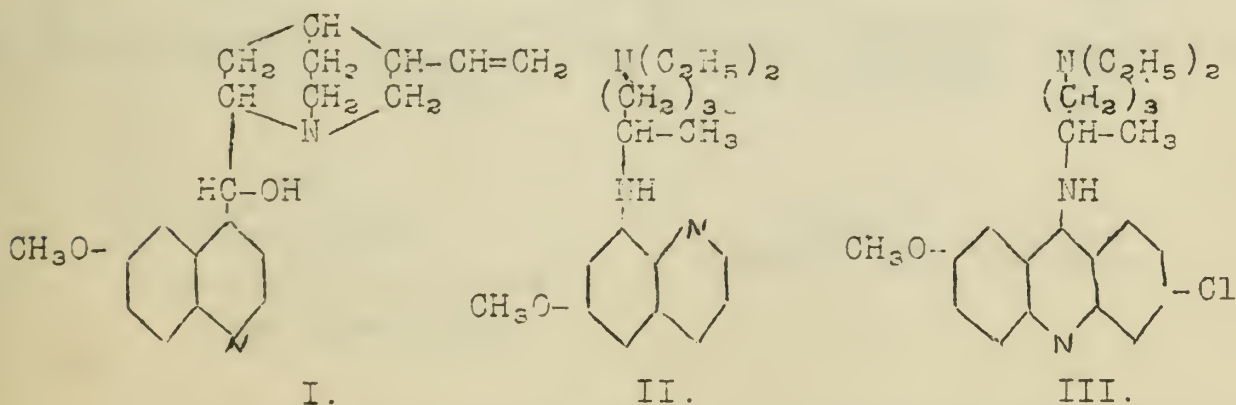


In this cycle arise the three forms of the malaria parasite--the sporozoites, the schizonts (asexual development forms) and the gametes (sexual forms).

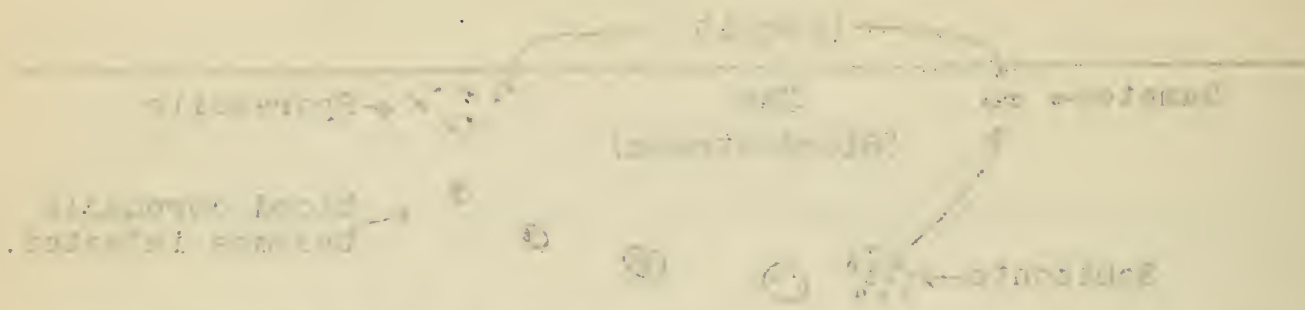
By the bite of the anopheles mosquito (with malaria tropical infection) the sporozoites arrive in man's blood. These quickly penetrate into the red corpuscles and transform themselves into the schizonts. The schizonts increase by simple division and cause the symptoms of malaria. Besides the schizonts another form of the parasite is produced, namely the gametes. They have no influence on the disease in man, but are important because they are the only form which can live in the organism of the mosquito. Therefore, the gametes complete the link in the cycle of malaria infection.

Quinine (I) was long the supreme remedy for malaria. It attacks the schizonts thereby destroying the symptoms of the disease, but it has no effect on the gametes or spread of the disease.

In 1926 Schulemann, Schönhöfer and Wingler (2) working for the I. G. Farbenindustrie (3) (4) discovered plasmochin (II) which has specific action on the gametes of tropical malaria. In 1930 Mauss and Mietzsch (5) working for the same company (6) (7) produced atebrin (III) which proved to be even more effective than quinine against the schizonts of tropical malaria.

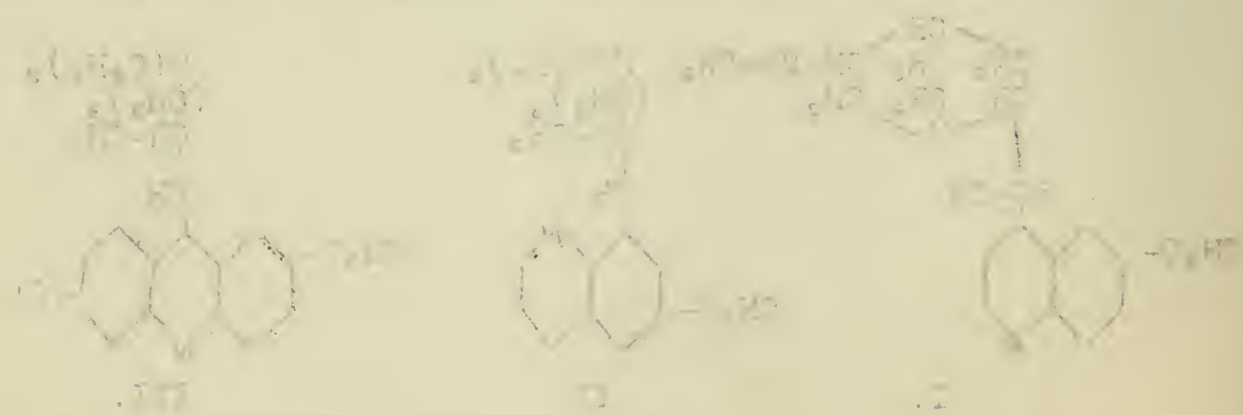


It is known that the active principle of the vitamin B₁₂ is a cobalt compound. The structure of the active principle is shown in the following diagram.



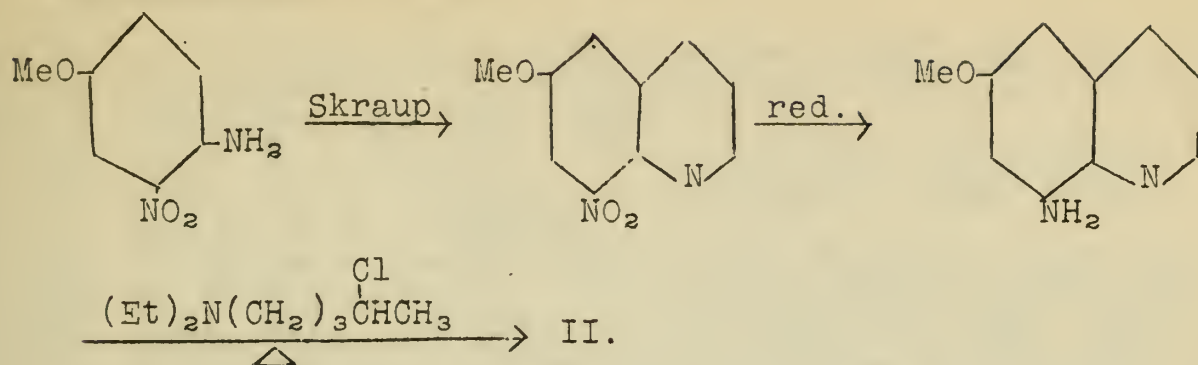
In this diagram, the cobalt atom is coordinated to the cyanide group, the dimethylamino group, and the complex ring system. The structure is labeled with various atoms and groups, including Co, CN, N(CH₃)₂, and various carbon and nitrogen atoms. The diagram illustrates the complex nature of the active principle of Vitamin B₁₂, which is a cobalt compound.

The structure of the active principle of Vitamin B₁₂ is shown in the following diagram. It is a cobalt compound, and its structure is highly complex, involving a central cobalt atom coordinated to various groups, including a cyanide group, a dimethylamino group, and a complex ring system. The diagram illustrates the intricate nature of this vitamin's active component.

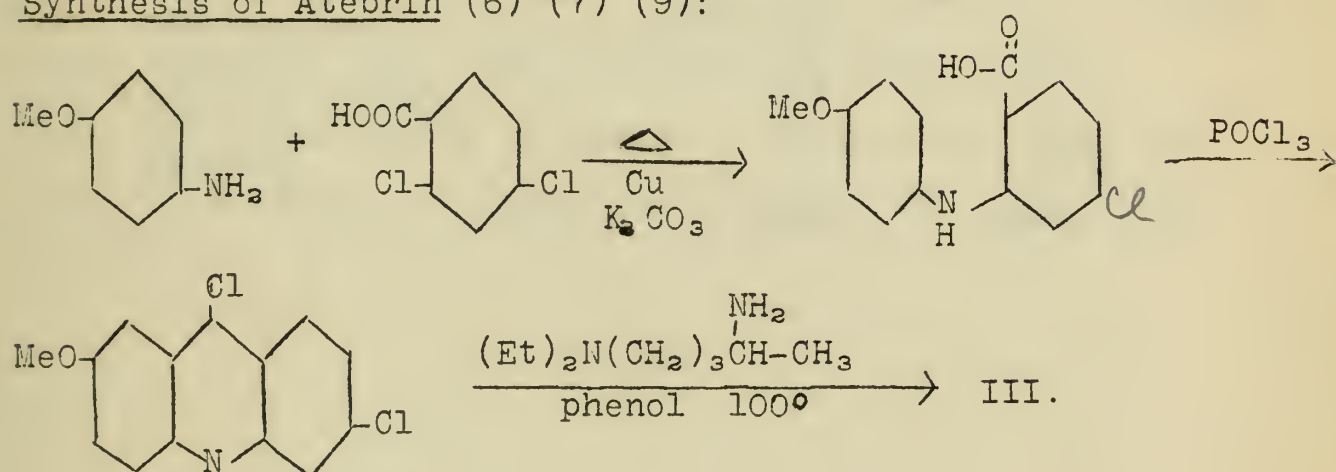


In the synthesis of the active principle of Vitamin B₁₂, the cobalt atom is coordinated to the cyanide group, the dimethylamino group, and the complex ring system. The structure is labeled with various atoms and groups, including Co, CN, N(CH₃)₂, and various carbon and nitrogen atoms.

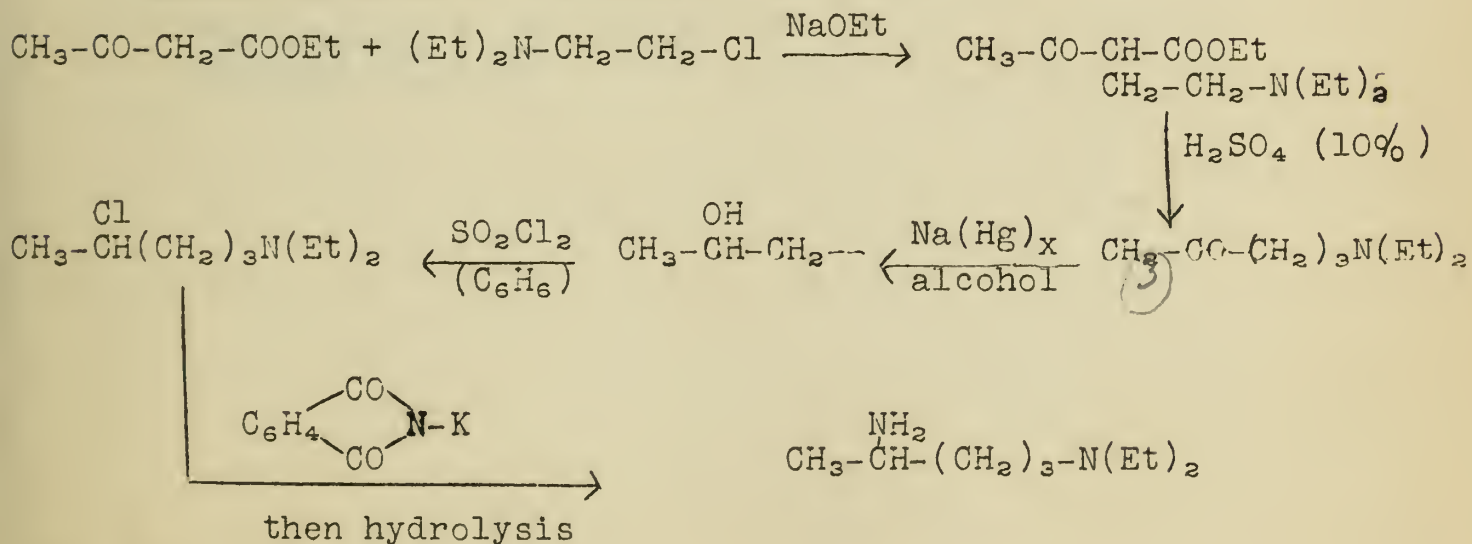
Synthesis of Plasmochin (3) (4) (9):



Synthesis of Atebrin (6) (7) (9):

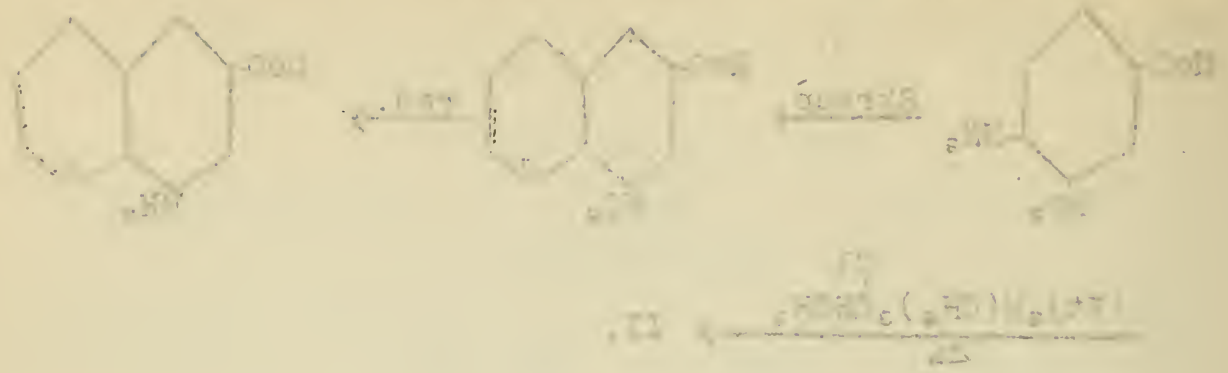


Synthesis of the side-chain (4) (9):

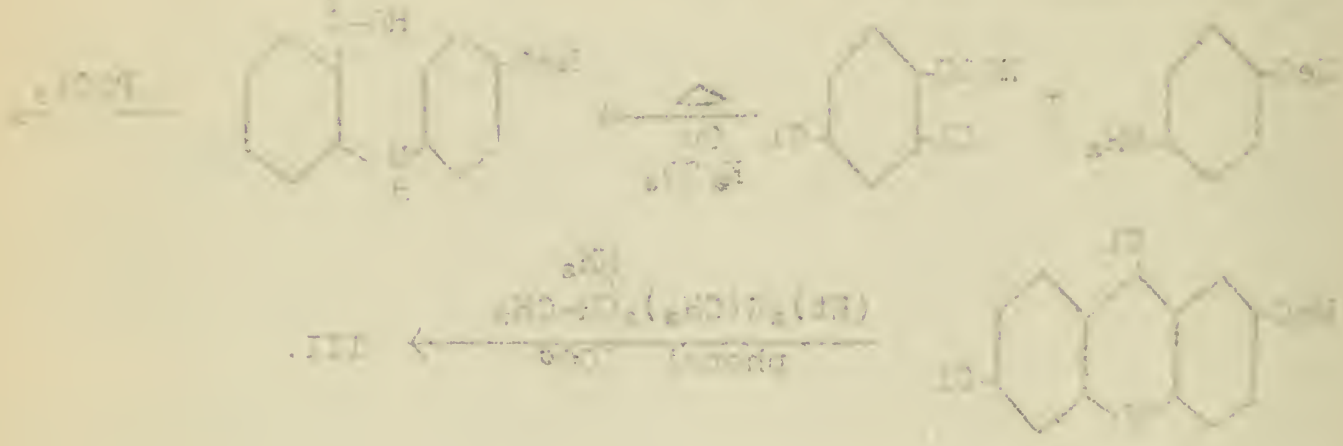


Other work in the field of synthetic antimalarials includes especially the work of the French chemist Fournieu (10) and the efforts of the British chemists, Barger and Robinson (11) and L. P. Walls (12).

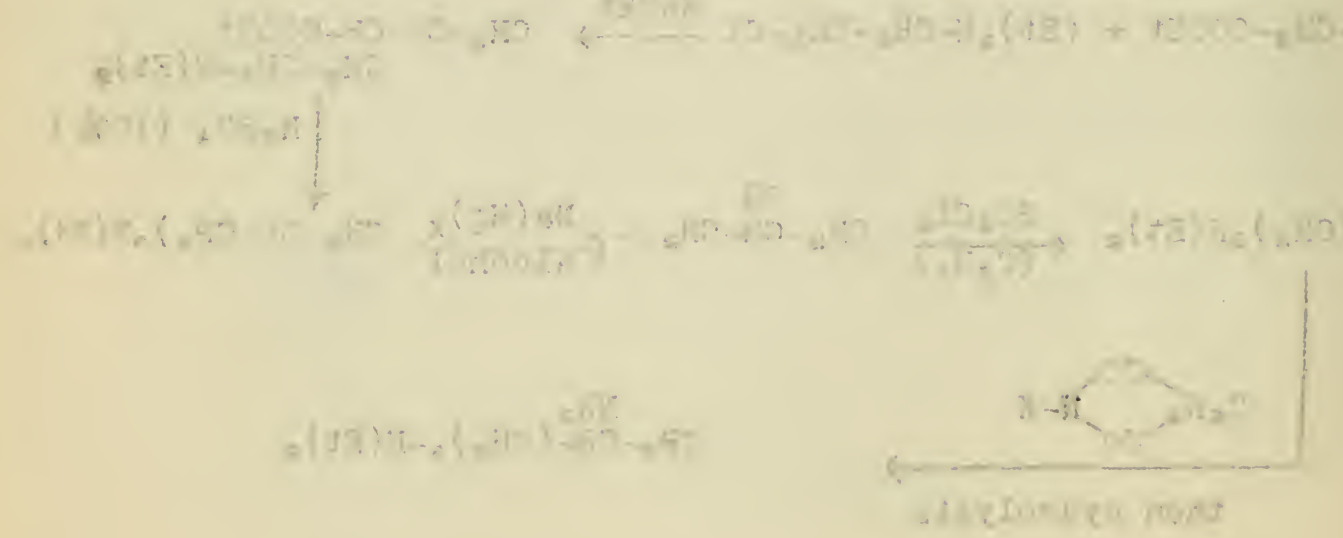
Synthesis of Phthalic Anhydride (12)



Synthesis of Anthracene (13)



Synthesis of the side-chain (14)



Other work in the field of synthetic anthracene derivatives is cited especially the work of the French chemist, Burger and Robinson and the efforts of the British chemist, Burger and Robinson (12) and M. F. Wain (13).

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2. W. Schulemann, F. Schönhofer and A. Wingler, *Klin. Wochschr.*, 11, 381 (1933).
3. D. R. P., 451,730, C. Z., 99 (I), 414 (1928).
4. Brit. Pat., 267,167, C. Z., 100 (I), 1965 (1929)
cf. D. R. P., 486,079.
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6. D. R. P., 553,072, C. Z., 103 (II), 1201 (1932).
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8. W. F. Oettingen, "Therapeutic Agents of Quinoline Group",
p. 108, Chem. Catalog Co., Inc., New York, (1933).
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Classe sci. math. nat., 1934, 176 (French), cf. 1934,
164 (German), C.A. 28, 4837 (1934).
10. Fourneau, *Ann. Inst. Pasteur*, 44, 503 (1930);
46, 534 (1931).
11. G. Barger and R. Robinson, *J. Chem. Soc.*, 1929 (III)
2947-68.
13. L. P. Walls, *J. Chem. Soc.*, 1934, 104; 1935, 1405.

Reported by E. E. Gruber
January 15, 1936.

SEMINAR TOPICS

II Semester 1935-36

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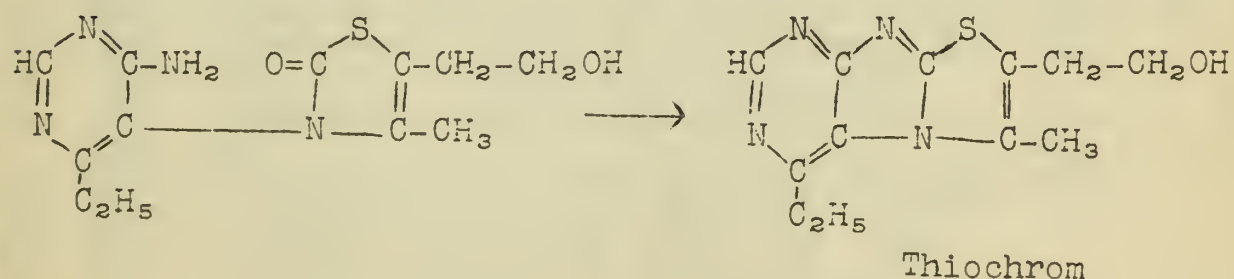
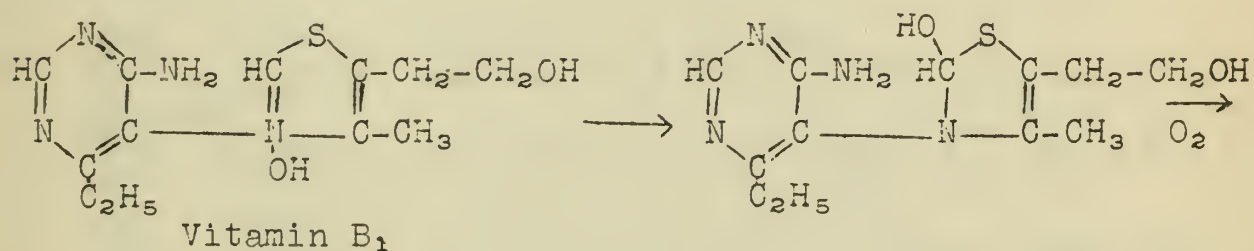
THIOCHROM FROM VITAMIN B₁

- R. Kuhn et al, Inst. Chem. Heidelberg
 1. Zeit. physiol. chem., 234, 196 (1935)
 2. Ber., 68, 2375 (1935)
 G. Barger, Medizin-chem. Inst. Univ. Edinburgh
 3. Ber., 68, 2357 (1935)
 4. Nature, 136, 259 (1935)
 A. Windaus et al., Allg. Chem. Univ. Göttingen
 5. Zeit. physiol. chem., 237, 98 (1935)

Kuhn¹ isolated a yellow dye from yeast, which in solution showed an intense blue fluorescence. He named this dye "Thiochrom" and found the formula to be C₁₂H₁₄ON₄S. The relation of this compound to Vitamin B₁ (also present in yeast) was studied because of the similarities in their formulas and because of the fact that fluorescent substances had been observed during the oxidation of the vitamin. Thiochrom itself has no vitamin B₁ activity.

Barger⁴ prepared Thiochrom from Vitamin B₁ in 33-40 per cent yields by oxidation with K₃Fe(CN)₆ in alkaline solution at 12-20°C.

Kuhn,² Barger,³ and Windaus,⁵ on the basis of further experiments, have each assigned the following structure to Thiochrom, and consider the following changes to take place during the oxidation.



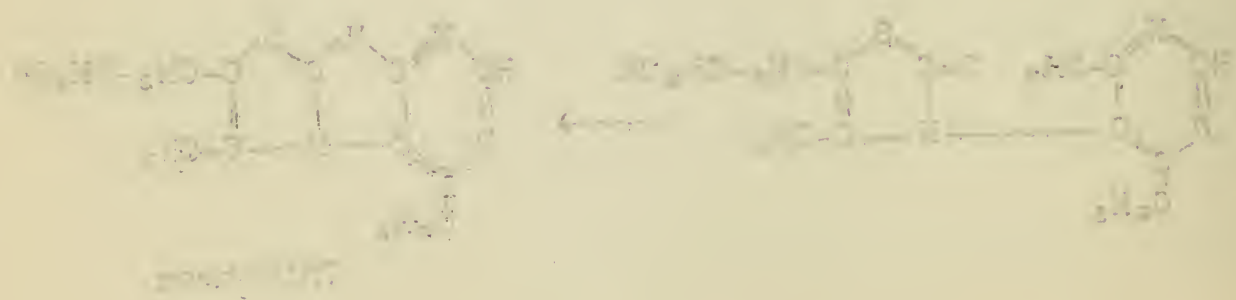
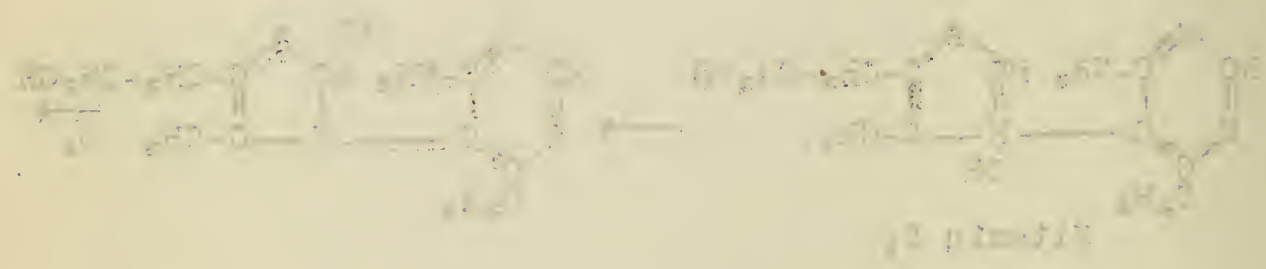
Reported by Meredith Sparks
 February 5, 1936

1. Kohn et al., *Ann. Chem. Phys.* (1931)
2. Kohn et al., *Ann. Chem. Phys.* (1931)
3. Kohn et al., *Ann. Chem. Phys.* (1931)
4. Kohn et al., *Ann. Chem. Phys.* (1931)
5. Kohn et al., *Ann. Chem. Phys.* (1931)
6. Kohn et al., *Ann. Chem. Phys.* (1931)
7. Kohn et al., *Ann. Chem. Phys.* (1931)
8. Kohn et al., *Ann. Chem. Phys.* (1931)
9. Kohn et al., *Ann. Chem. Phys.* (1931)
10. Kohn et al., *Ann. Chem. Phys.* (1931)

The authors have shown that the vibration of the molecule is not a simple harmonic motion, but a complex motion which can be described by a series of terms. The first term is the harmonic motion, and the other terms are the anharmonic motions. The anharmonic motions are of two kinds: the first kind is the anharmonic motion of the first order, and the second kind is the anharmonic motion of the second order. The anharmonic motion of the first order is the anharmonic motion of the first order, and the anharmonic motion of the second order is the anharmonic motion of the second order.

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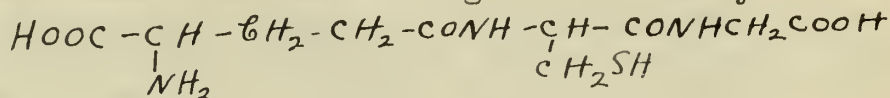


Chas. Rob't. Harrington and Thomas H. Mead
Department of Pathological Chem., Univ. College Hosp.,
Medical School, London.

In 1921, Hopkins¹ isolated glutathione from yeast, and muscle and liver tissue, and gave evidence to show that the substance is a dipeptide containing glutamic acid and cysteine. In 1923, Omastel, Tunncliffe, and Stewart² obtained evidence which led them to believe that glutathione is γ -glutamylcystein. Later, in 1925, Stewart and Tunncliffe³ believed they had positive evidence for such a structure, by its supposed synthesis.

Hunter and Eagles (1927)⁴, obtained a third amino acid from their glutathione preparations, thereby giving evidence for the incorrectness of the above structure. In 1930, Hopkins⁵ reinvestigated the problem, and, by a better method for separation of the peptide, obtained crystalline glutathione. He then showed it to be a tripeptide of glutamic acid, cysteine, and glycine. At about the same time, Kendall et al. reached the same conclusion by a different method for separation of the peptide.

Experimental evidence^{2,5-11} established the structure of glutathione as γ -glutamylcysteylglycine. In 1935, Harrington and Meade confirmed this structure for glutathione by its synthesis¹²⁻¹⁶.



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1. 1921 - Hopkins, Biochem. J., 15, 286.
2. 1923 - Omastel, Stewart, and Tunncliffe, Biochem. J., 17, 586.
3. 1925 - Stewart and Tunncliffe, Biochem. J., 19, 207.
4. 1927 - Hunter and Eagles, J. Biol. Chem., 72, 147.
5. 1930 - Hopkins, J. Biol. Chem., 84, 269.
6. 1930 - Kendall, McKenzie and Mason, J. Biol. Chem., 84, 657.
7. 1930 - Kendall, McKenzie and Mason, J. Biol. Chem., 87, 55.
8. 1930 - Kendall, McKenzie and Mason, J. Biol. Chem., 88, 409.
9. 1930 - Pirie and Pinkey, J. Biol. Chem., 84, 321.
10. 1930 - Nicolet, J. Biol. Chem., 83, 389.
11. 1930 - Grassmann, Dickerhoff and Eibeler, Z. Physiol. Chem., 189, 112.
12. 1935 - Harrington and Mead, Biochem. J., 29, 1602.
13. 1932 - Bergman and Zervas, Ber., 65, 1192.
14. 1933 - Bergman and Zervas, Ber., 66, 1288.
15. 1931 - Lamb and Robson, Biochem. J., 25, 1231.
16. 1935 - Melville, Biochem. J., 29, 179.

Chas. A. B. Hartshorn and Thomas H. Jones
Department of Pathological Chemistry, Johns Hopkins Hospital
Baltimore, Maryland

In 1907, Hartshorn, Jones and Jones, in a paper published in the Journal of Biological Chemistry, reported the results of their studies on the metabolism of the amino acid, glycine. In this paper, they presented evidence that glycine is a direct precursor of the amino acid, alanine. In 1907, Hartshorn, Jones and Jones, in a paper published in the Journal of Biological Chemistry, reported the results of their studies on the metabolism of the amino acid, glycine. In this paper, they presented evidence that glycine is a direct precursor of the amino acid, alanine. In 1907, Hartshorn, Jones and Jones, in a paper published in the Journal of Biological Chemistry, reported the results of their studies on the metabolism of the amino acid, glycine. In this paper, they presented evidence that glycine is a direct precursor of the amino acid, alanine.

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1. 1907 - Hartshorn, Jones and Jones, J. Biol. Chem., 1, 281.
2. 1907 - Hartshorn, Jones and Jones, J. Biol. Chem., 1, 281.
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7. 1907 - Hartshorn, Jones and Jones, J. Biol. Chem., 1, 281.
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10. 1907 - Hartshorn, Jones and Jones, J. Biol. Chem., 1, 281.
11. 1907 - Hartshorn, Jones and Jones, J. Biol. Chem., 1, 281.
12. 1907 - Hartshorn, Jones and Jones, J. Biol. Chem., 1, 281.
13. 1907 - Hartshorn, Jones and Jones, J. Biol. Chem., 1, 281.
14. 1907 - Hartshorn, Jones and Jones, J. Biol. Chem., 1, 281.
15. 1907 - Hartshorn, Jones and Jones, J. Biol. Chem., 1, 281.
16. 1907 - Hartshorn, Jones and Jones, J. Biol. Chem., 1, 281.

The Peroxide Effect in the Addition of Hydrogen Bromide to Unsaturated Compounds

3

Within the past three years Kharasch and coworkers (at the University of Chicago) have published the results of their systematic investigation of the various physical and chemical factors influencing the direction of addition of hydrogen bromide to a series of aliphatic compounds containing unsaturation involving a terminal carbon atom, e.g., allyl bromide,¹ vinyl bromide,² propylene,³ 4,4-dimethylpentene-1,⁴ vinyl chloride,⁵ butene-1,⁶ pentene-1,⁷ allyl acetic acid,⁸ and isobutylene,^{9,10}. They have been able to make some very interesting generalizations, to which they have found no exceptions. These may be briefly summarized as follows:

1. The Peroxide Effect.--The presence or absence of peroxides in the reaction mixture is the sole factor determining the direction of the addition. In the absence of peroxides the addition is according to Markownikoff's rule (called "normal" addition), whereas even small amounts of peroxides cause terminal addition of the bromine atom (called "abnormal" or "peroxide-catalyzed" addition). In the presence of peroxides the two reactions are competitive, but the peroxide-catalyzed reaction is normally much the faster.
2. The Temperature Effect.--Increased temperature causes an increase in the velocity of both reactions. Their temperature coefficients may differ, however, that of the peroxide-catalyzed reaction usually being the higher.
3. The Solvent Effect.--The solvent has no direct effect on the direction of addition but may affect the stability of peroxides, resist the effect of oxygen, or affect the relative velocities of the two competing reactions.
4. The Light Effect.--Light of all wave lengths accelerates both reactions, but usually the peroxide-catalyzed reaction is accelerated much more than the normal one. This serves to amplify the effect of small amounts of peroxides.
5. The Effect of Metallic Salts.--Anhydrous ferric and aluminum halides have a tremendous accelerating effect upon the normal addition. Copper salts have a slight antioxidant and accelerating effect.
6. The Effect of Surface Catalysts.--Broken pyrex, glass wool, asbestos, and silica gel were without effect on either the direction or velocity of the reaction.

Different unsaturated compounds show considerable variation in their susceptibility to the peroxide effect and in the ease with which they form peroxides by oxidation. The vinyl halides were the most sensitive, whereas propylene, butene-1, and isobutylene were the least sensitive.

The Hydrogen Peroxide Test for Hydrogen Peroxide

Hydrogen peroxide is a colorless liquid with a strong, irritating odor. It is used in a variety of applications, including as a disinfectant, a bleaching agent, and a component in many household products. The hydrogen peroxide test is a simple method for identifying the presence of hydrogen peroxide in a sample. This test involves the addition of a small amount of the sample to a solution of potassium iodide and sulfuric acid. If hydrogen peroxide is present, it will oxidize the iodide ions to iodine, which will then react with the sulfuric acid to form a yellow-orange precipitate of elemental iodine. The intensity of the color is proportional to the concentration of hydrogen peroxide in the sample.

The test is performed by adding a few drops of the sample to a test tube containing a solution of potassium iodide and sulfuric acid. The mixture is then shaken and allowed to stand for a few minutes. A yellow-orange precipitate will form if hydrogen peroxide is present. The color of the precipitate can be used to estimate the concentration of hydrogen peroxide in the sample. A color chart can be used to compare the color of the precipitate to known concentrations of hydrogen peroxide.

The test is a simple and reliable method for identifying the presence of hydrogen peroxide in a sample. It is commonly used in laboratories and in the field for the identification of unknown substances.

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In 1935 Harris and Smith¹¹ showed that a terminal triple bond may be subject to exactly the same sort of peroxide effect by their investigation of the addition of HBr to Δ^{10} -undecynoic acid. They also found a decided peroxide effect in the addition of HBr to undecenoic acid, but found that molecular oxygen was necessary, in addition to a peroxide, in order to produce terminal addition.

The only types of unsaturated compounds in which Kharasch has thus far been able to reverse the direction of addition of HBr, by the use of peroxides or antioxidants, are those in which the double bond is either adjacent to a carboxyl group (e.g. crotonic acid) or does not involve a terminal carbon atom (e.g. pentene-2).

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1. Kharasch and Mayo, J. Am. Chem. Soc., 55, 2468 (1933).
2. Kharasch, McNab, and Mayo, J. Am. Chem. Soc., 55, 2521 (1933).
3. Kharasch, McNab, and Mayo, J. Am. Chem. Soc., 55, 2531 (1933).
4. Kharasch, Hannum, and Gladstone, J. Am. Chem. Soc., 56, 244 (1934).
5. Kharasch and Hannum, J. Am. Chem. Soc., 56, 712 (1934).
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7. Kharasch, Hinckley, and Gladstone, J. Am. Chem. Soc., 56, 1642 (1934).
8. Kharasch and McNab, J. Soc. Chem. Ind., 54, 989 (1935).
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10. Kharasch and Potts, J. Am. Chem. Soc., 58, 57 (1935).
11. Harris and Smith, J. Chem. Soc., 1935, 1572.

Reported by F. E. Condo
February 12, 1936.

It is noted that the results of the analysis of the data for the year 1955 are in general agreement with those for the year 1954. The only difference is that the results for the year 1955 are slightly higher than those for the year 1954. This is due to the fact that the data for the year 1955 are more complete than those for the year 1954.

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1. Johnson and Smith, J. A. (1955).
2. Johnson and Smith, J. A. (1955).
3. Johnson and Smith, J. A. (1955).
4. Johnson and Smith, J. A. (1955).
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Reported by R. E. Jones
January 15, 1956

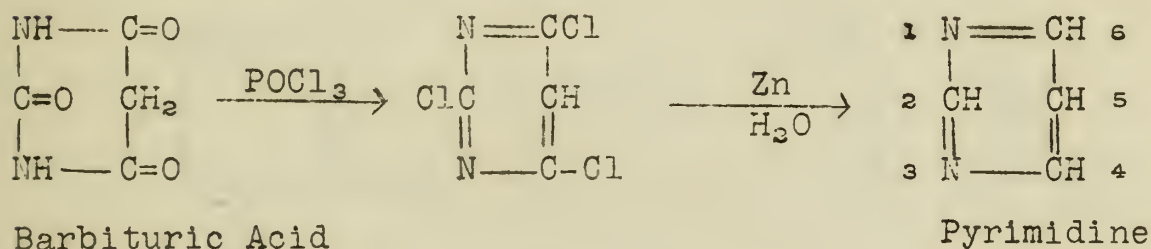
PYRIMIDINES

References:

- Caldwell and Ziegler, J. Am. Chem. Soc., 58, 78 (1936).
 T. B. Johnson, J. Am. Chem. Soc., 57, 2252 (1935).
 T. B. Johnson and D. Hahn, Chem. Rev., 13, 193 (1933).
 Levene, Am. Chem. Soc. Monograph, No. 56, 35-74.

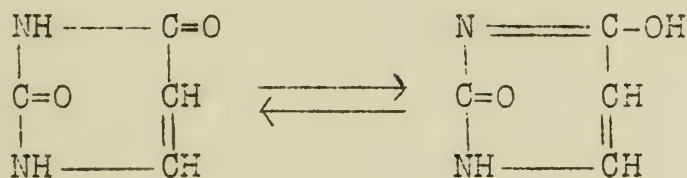
Pyrimidines have been of interest for a number of years due to their presence in animal and plant cells as a constituent of nucleic acids. Recently, the interest in this field has been renewed since the structure proposed for vitamin B₁ contains the pyrimidine ring.

Pyrimidine may be synthesized in the following manner:

Properties

Pyrimidines are meta-diazines and are basic as would be expected from their structural relationship to pyridine. The introduction of oxygen into the nucleus, however, diminishes the basicity.

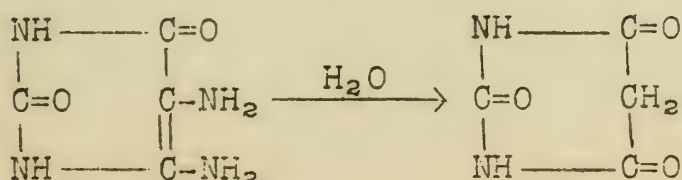
For example:



Uracil

Uracil is a weak acid while barbituric acid is sufficiently acidic to give a good neutral equivalent.

Many of the properties of the oxy- and amino-pyrimidines arise from their ability to tautomerize from the lactam and amine forms to the lactim and imine structures. The preparation of pyrimidine from barbituric acid is an example of the former. An example of the latter is the following:

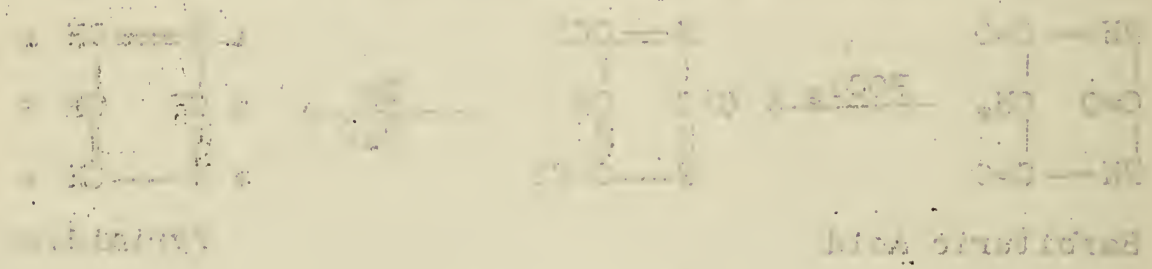


References:

Calhoun and Johnston, J. Am. Chem. Soc. 54, 1000 (1932).
T. E. Johnston and J. E. Johnston, J. Am. Chem. Soc. 54, 1000 (1932).
Larson, J. Am. Chem. Soc. 54, 1000 (1932).

Pyrimidine and its derivatives are of interest for a number of reasons. Due to their presence in nucleic acids and their role in the synthesis of nucleic acids, pyrimidines are of interest in the study of the chemical and physical properties of the nucleic acids. Pyrimidine is a heterocyclic compound consisting of a six-membered ring with two nitrogen atoms.

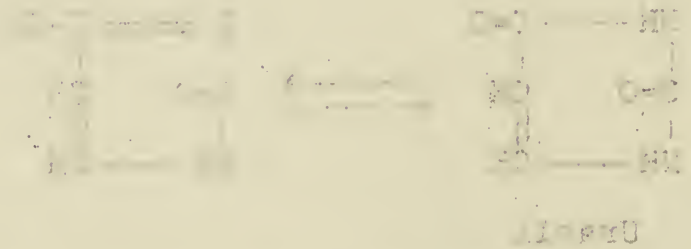
Pyrimidine may be synthesized in the following manner:



Properties:

Pyrimidine is a white crystalline solid with a melting point of 100°C. It is soluble in water and has a strong odor. The introduction of groups into the pyrimidine ring system can alter its properties.

For example:

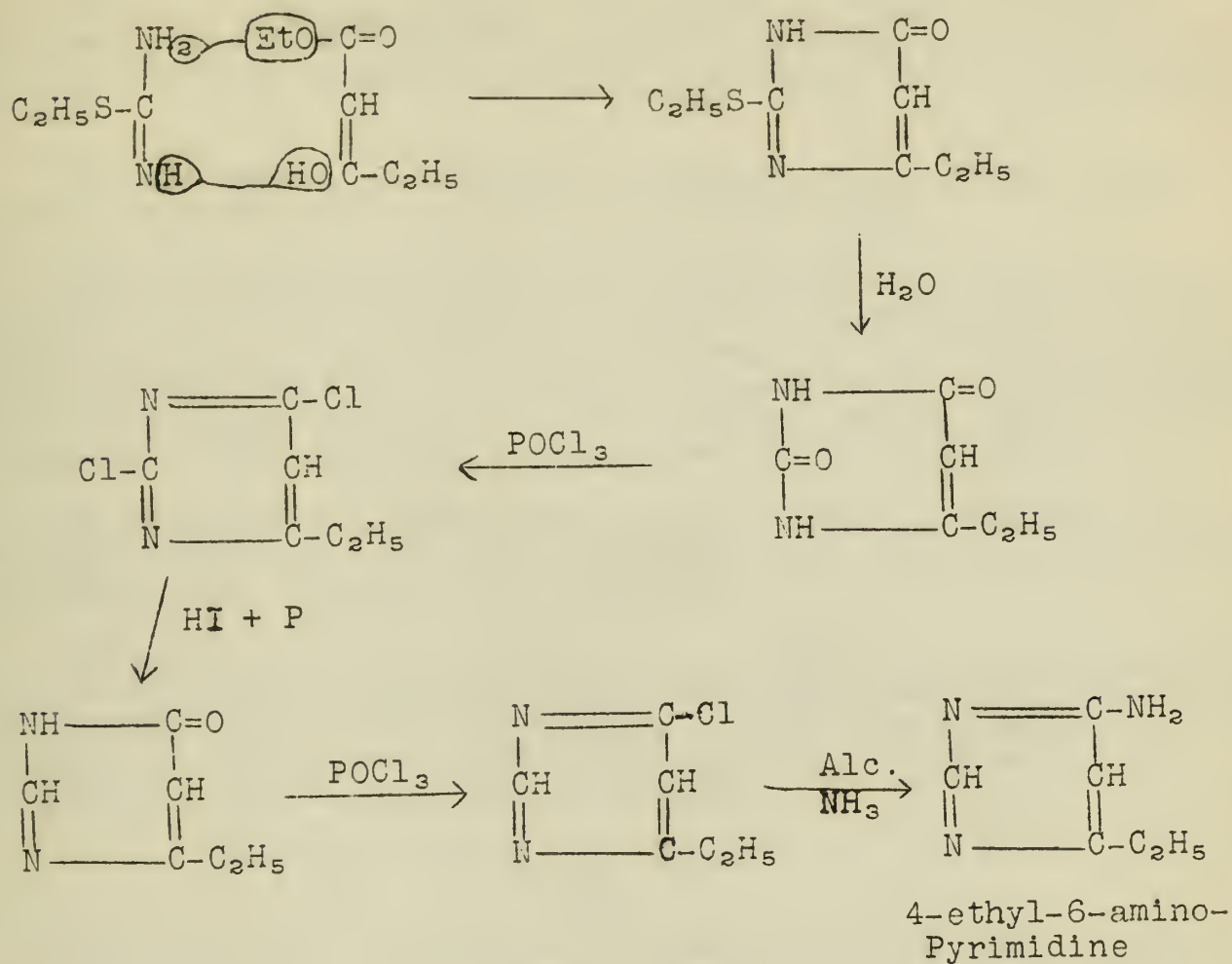


Urea is a weak acid with a pKa of 10.3. It is soluble in water and has a strong odor. It is used in the synthesis of many organic compounds.

Many of the properties of the urea and urea derivatives arise from their ability to form hydrogen bonds. The hydrogen bonds form between the nitrogen and oxygen atoms of the urea molecule. The hydrogen bonds are responsible for the high boiling point and the high melting point of urea. An example of the hydrogen bonds is shown below:



The following, which represents a general method, is a synthesis for the pyrimidine likely present in Vitamin B₁.



Reported by H. H. Hully
February 12, 1936.

all conditions except the above, the following conditions apply:
1. The following conditions apply to the following conditions:



10'0"



10'0"



10'0"

10'0"

Kögl and Boer, Rijks Univ., Utrecht
 Rec. Trav. Chim., 54, 779 (1935)

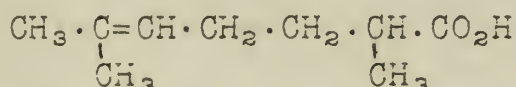
Perezon is the orange-yellow coloring matter obtained from the roots of Perezia Adnata. The plant is found in Mexico. The material is of interest because of its physiological action. It has a strong purgative action, for which it is much used in Mexico.

Perezon was first isolated in 1885 by M. C. Wild, by an alcoholic extraction of the roots of the plant.

Analysis and molecular weight determinations show it to be $C_{15}H_{20}O_3$. Two of the oxygens belong to a quinone system and the third a phenolic hydroxyl. The presence of one double bond was shown by the addition of bromine. Treatment with aniline yielded an anilido compound which, on hydrolysis, yields oxy-perezon, $C_{15}H_{20}O_4$. This compound contains two phenolic groups.

On ozonization α, β -diketo butyric acid is obtained. On warming oxy-perezon with concentrated H_2SO_4 , water is split out and perezinon, $C_{15}H_{18}O_3$, is obtained.

Oxidation of perezon with H_2O_2 in alkaline solution yields acetic acid and a higher boiling acid whose analysis and neutral equivalent showed it to be $C_9H_{16}O_2$. There are 91 possible isomers of this nonane acid. Kögl was able to show that the acid was identical with the following:

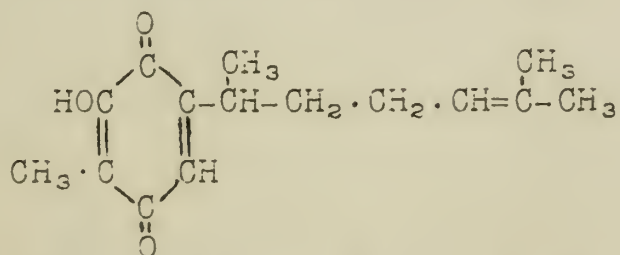


Proof of the positions of the side-chains on the quinone ring were shown by the following reactions:

Oxidation of tetramethoxy-leuko-dihydroxy-perezon yielded tetramethoxy-tere-phthalic acid.

Distillation with zinc dust of perezon gave an oil which on oxidation yielded tere-phthalic acid.

From the evidence which he had Kögl assigned the following structure to perezon:



Kögl states that this is the first natural product which has been found that contains a quinone of the sesquiterpene type.

...and the ...

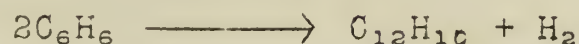
Synthesis of Diphenyl, 2,2'-Dipyridyl, 2,2'-
Diquinolyl and Some of Their Homologs

Wibaut and coworkers: Rec. Trav. Chim., 54, 275 (1935)
 " " " , 54, 804 (1935)
 " " " , 54, 807 (1935)
 " " " , 53, 584 (1934)
 " " " , 53, 417 (1934)

Place: Laboratory for Organic Chemistry, University of
Amsterdam.

Previous Work:

Diphenyl was prepared by heating benzene in a steel autoclave at 440° and 190 atmcs. in the presence of nickel or iodine.



By the use of the same procedure 2,2'-dipyridyl, 2,2'-diquinolyl and 6,6'-dimethyl-2,2'-dipyridyl were synthesized. Some compounds of this type form highly colored complexes with ferrous salts. It was hoped to determine the conditions necessary for the formation of the complex in a molecule of this type. The 2,2'-linkage is necessary but not the sole factor.

2,2'-dipyridyl-3,3'-dicarboxylic acid was synthesized in order to attempt its resolution. Preliminary attempts failed but this work is being carried further.

The conditions for maximum yields for the dipyridyl were not as vigorous as those for diphenyl; consequently the pyridine nucleus must be more active than the benzene nucleus.

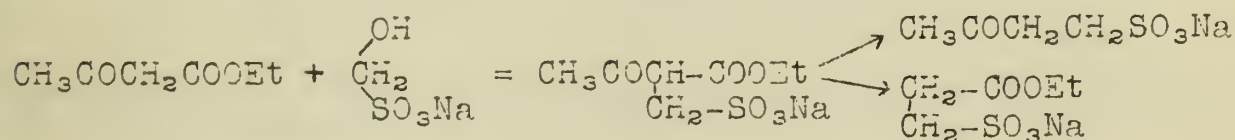
Reported by R. F. Miller
February 19, 1936

1. Raschig and Prahl, Ludwigshafen a. Rh.
Ber., 59, 859 (1925)
" 59, 2025 (1926)
" 61, 179 (1928)
Ann., 443, 365 (1926)
2. Backer and Mulder, Groningue.
Rec. Trav. Chim., 53, 454 (1933)
" " " 53, 1120 (1934)
3. Lauer and Langkammerer,
J. Am. Chem. Soc., 57, 2360 (1935)

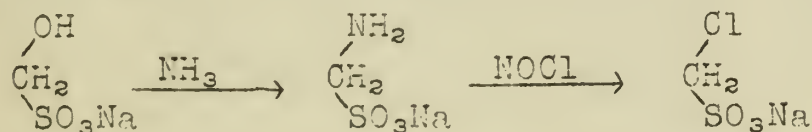
Early evidence on the structure of sulfite addition compounds consisted in the preparation of supposedly hydroxy-sulfonic acids which were not identical with the corresponding sulfite addition compounds.

Raschig and Prahl¹ in a series of investigations were able to show that previous workers had made the mistake of preparing, not the supposed hydroxysulfonic acids, but entirely different compounds. These were then compared with the sulfite addition compounds with the result that the sulfite additions were not found to be sulfonic acids.

In addition they have shown that formaldehyde sulfite adds to acetoacetic ester and subsequent cleavage always results in a sulfonic acid.

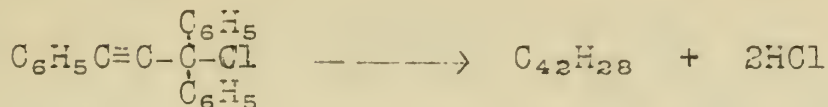


Further evidence in support of the sulfonic acid structure was brought out by Backer and Mulder,² who showed that treatment of the addition compound of formaldehyde and sulfite with NH_3 followed by NOCl resulted in a chlorosulfonic acid.



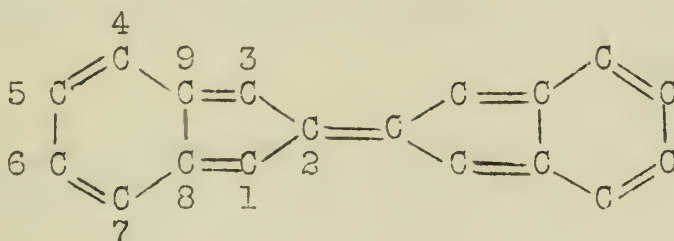
Lauer and Langkammerer,³ with iodoform and the formaldehyde addition product as different starting materials, have built up sulfonic acids which they have shown to be identical, so establishing the identity of such addition as a hydroxysulfonic acid.

In 1936, Moreau¹ discovered a red hydrocarbon, rubrene, by the action of heat on diphenylphenylethynechloromethane:



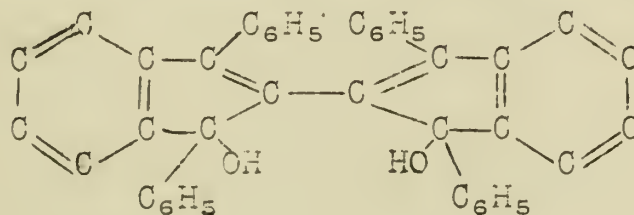
This orange-red hydrocarbon was slightly soluble in organic solvents, fluoresced, nitrated and sulfonated giving several isomers, and reacted with oxygen in the presence of light to give a dissociable dioxide. It had a characteristic absorption peak² at 4650, 4950 and 5300 Å. Vigorous oxidation gave a 50 per cent yield of *o*-dibenzoylbenzene, some benzoic and phthalic acids.

Various mechanisms³ and structures have been offered for rubrene. Several methods of preparation have been offered and many substituted rubrenes have been made.⁴ Willemart and Moreau⁵ and coworkers, from the above information and the various reactions that it undergoes, have assumed that it is a dibenzobifulvene.



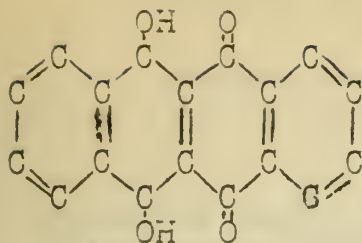
The continuous chain of conjugation as well as the *o*-quinoid structure contribute to its color.

Marvel and Eck⁶ synthesized Bis-2,2'-(1,3-diphenylindol-3)

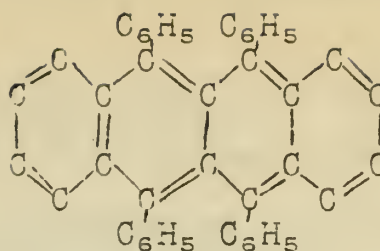


which should have been identical with dihydroxytetraphenylrubrene; however, the physical and chemical behavior of the compound did not agree with those of the dihydroxytetraphenylrubrene.

Recently, Dufraisse⁷ synthesized 9,10,11,12-tetraphenyl-naphthacene and has shown that this compound is identical with tetraphenylrubrene. The compound was prepared as follows:



1. $\text{C}_6\text{H}_5\text{MgBr}$
2. Dehydration
3. $\text{C}_6\text{H}_5\text{MgBr}$
4. Reduction

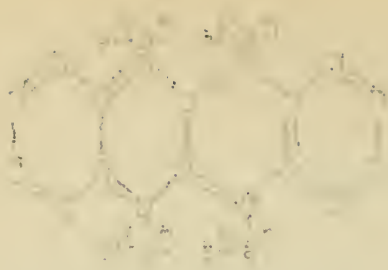


9,10-dihydroxynaphthacenequinone-11,12

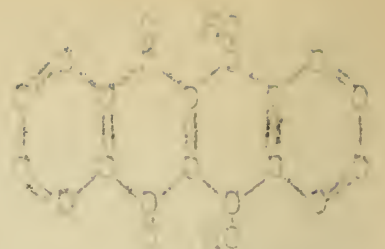
Since this compound alters the structural formula of rubrene it must also alter the mechanism of formation and the explanation of its reactions.

1. Moreau and Dufraisse, *Compt. Rend.*, 182, 1440 (1926)
Bull. Soc. Chim., (4), 33, 934 (1923)
2. Dufraisse, *Bull. Soc. Chim.*, 53, 739-849 (1933)
3. Willemart, *Compt. Rend.*, 187, 385 (1928)
4. Dufraisse and others, *Compt. Rend.* 191, 619 (1930)
192, 1389 (1931)
194, 1664 (1932)
195, 963 (1932)
5. Willemart, *Compt. Rend.*, 187, 385 (1928)
6. Marvel and Eck, *J. Am. Chem. Soc.*, 57, 1898 (1935)
7. Dufraisse and Velluz, *Compt. Rend.*, 201, 394 (1935)

Reported by L. R. Drake
 February 26, 1936.



1. 1,2,3,4,5,6-hexachlorocyclohexane
2. 1,2,3,4,5,6-hexachlorocyclohexane
3. 1,2,3,4,5,6-hexachlorocyclohexane



1,2,3,4,5,6-hexachlorocyclohexane

Since this compound is a derivative of benzene, it is expected to exhibit the same chemical properties as benzene. It is also expected to be a liquid at room temperature and to be insoluble in water.

1. 1,2,3,4,5,6-hexachlorocyclohexane, 1,2,3,4,5,6-hexachlorocyclohexane, 1,2,3,4,5,6-hexachlorocyclohexane
2. 1,2,3,4,5,6-hexachlorocyclohexane, 1,2,3,4,5,6-hexachlorocyclohexane, 1,2,3,4,5,6-hexachlorocyclohexane
3. 1,2,3,4,5,6-hexachlorocyclohexane, 1,2,3,4,5,6-hexachlorocyclohexane, 1,2,3,4,5,6-hexachlorocyclohexane
4. 1,2,3,4,5,6-hexachlorocyclohexane, 1,2,3,4,5,6-hexachlorocyclohexane, 1,2,3,4,5,6-hexachlorocyclohexane
5. 1,2,3,4,5,6-hexachlorocyclohexane, 1,2,3,4,5,6-hexachlorocyclohexane, 1,2,3,4,5,6-hexachlorocyclohexane
6. 1,2,3,4,5,6-hexachlorocyclohexane, 1,2,3,4,5,6-hexachlorocyclohexane, 1,2,3,4,5,6-hexachlorocyclohexane
7. 1,2,3,4,5,6-hexachlorocyclohexane, 1,2,3,4,5,6-hexachlorocyclohexane, 1,2,3,4,5,6-hexachlorocyclohexane

ADDITION OF GRIGNARD REAGENTS TO β -KETO ALDEHYDES

Meyer, R. E., Helv., 18, 101, 279, 282, 305, 461,
467, 470 (1935)

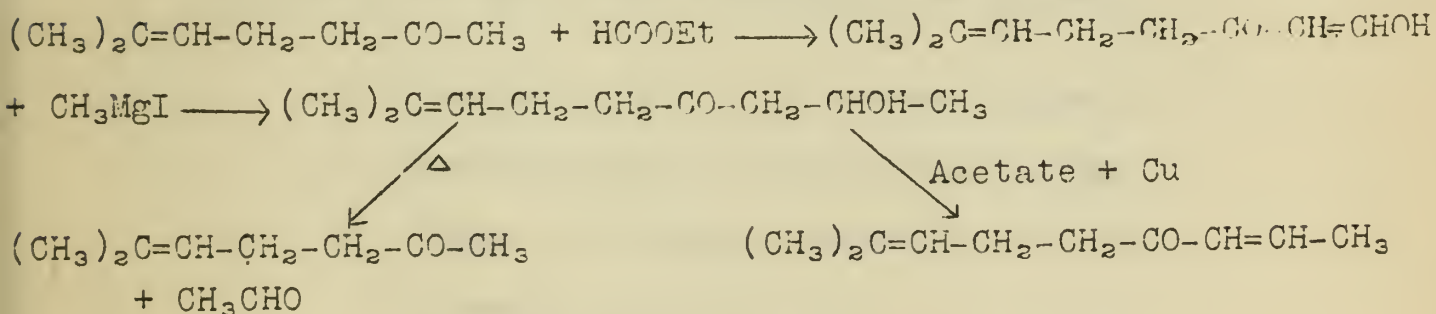
Basel, Institute for Inorganic Chemistry.

Previous work: Preservation and determination of citronellal; titrimetric determination of aldehydes and ketones.

The frequent 1,4 addition of the Grignard reagent to ordinary α,β -unsaturated ketones was studied by Kohler.

When Meyer reacted methylmagnesiumiodide with the oxymethylene derivative of 6-methyl-5-hepten-2-one, he obtained instead of the desired hydroxy aldehyde, which would give citral by dehydration, an oil which gave no crystalline phenylhydrazone or anil, positive tests with Tollen's and Schiff's reagents, and on dehydration by distillation gave besides the corresponding unsaturated compound, 60 per cent of 6-methyl-5-hepten-2-one and acetaldehyde. Careful dehydration by warming the acetate with powdered copper gave chiefly the corresponding compound.

To determine the structure of this product, the same reactions were carried out with 6-methylheptan-2-one and the product oxidized with permanganate, giving δ -methylcaproic acid. The reactions must then have been:



Both the positive aldehyde tests and the splitting of the product of the action of the Grignard reagent were ascribed to the β -hydroxyketone structure.

Although the absence of 1,2 addition prevents the formation of citral by this process, the 1,4 addition gives a fairly satisfactory way of augmenting a methyl ketone by an ethylidene group in compounds which do not readily undergo the Claisen-Schmidt reaction.

Reported by Frank C. McGrew
March 4, 1936.

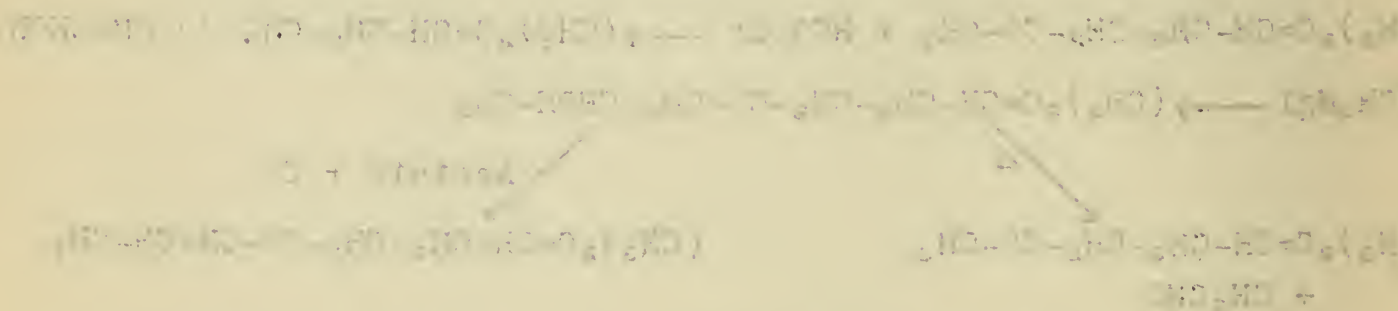
Copyright, 1951, by the American Chemical Society
 1951, 1952, 1953, 1954, 1955, 1956, 1957, 1958, 1959, 1960, 1961, 1962, 1963, 1964, 1965, 1966, 1967, 1968, 1969, 1970, 1971, 1972, 1973, 1974, 1975, 1976, 1977, 1978, 1979, 1980, 1981, 1982, 1983, 1984, 1985, 1986, 1987, 1988, 1989, 1990, 1991, 1992, 1993, 1994, 1995, 1996, 1997, 1998, 1999, 2000, 2001, 2002, 2003, 2004, 2005, 2006, 2007, 2008, 2009, 2010, 2011, 2012, 2013, 2014, 2015, 2016, 2017, 2018, 2019, 2020, 2021, 2022, 2023, 2024, 2025

Physical and chemical properties of 2-ethyl-2-butene and its hydrogenation products.

The present work is a continuation of the previous work on the hydrogenation of 2-ethyl-2-butene.

When 2-ethyl-2-butene is hydrogenated over a nickel catalyst, the product is 2-methyl-2-butanol. This reaction is reversible, and the equilibrium constant is 1.0. The reaction is exothermic, and the heat of reaction is -12.5 kcal/mole. The reaction is first order with respect to 2-ethyl-2-butene and zero order with respect to hydrogen. The reaction is inhibited by carbon monoxide and sulfur compounds. The reaction is accelerated by nickel, cobalt, and iron catalysts. The reaction is also accelerated by nickel, cobalt, and iron catalysts in the presence of a small amount of hydrogen. The reaction is also accelerated by nickel, cobalt, and iron catalysts in the presence of a small amount of hydrogen. The reaction is also accelerated by nickel, cobalt, and iron catalysts in the presence of a small amount of hydrogen.

The following table gives the results of the experiments on the hydrogenation of 2-ethyl-2-butene over a nickel catalyst.



Both the positive and negative results of the experiments on the hydrogenation of 2-ethyl-2-butene are discussed in the text.

The following table gives the results of the experiments on the hydrogenation of 2-ethyl-2-butene over a nickel catalyst.

Raman Spectra in Organic Chemistry

Kohlrausch and Pongratz, Monatsh, 64, 361 (1934)

Gredy, Ann. Chim., 11^e, 4 (1935)

Gehman and Osterhof, J. Am. Chem. Soc., 58,
215, 1936)

When monochromatic light (i.e., light of a single frequency) is passed through a compound or its solution, one observes not only the incident beam but also several other frequencies whose values are characteristic of the atomic bindings in the molecule. These studies are admirably adapted to the settlement of important organic questions of which the following are typical:

1. Determination of cis-trans isomers.
2. Determination of functional groups.
3. Types of linkages present; semi-polar
normal covalent, etc.
4. Strength of atomic bindings.

Reported by R. T. Arnold

March 4, 1936.

Kohlrausch and Harnack, *Monatsh.*, **24**, 381 (1904)

Greeff, *Ann. Chem.*, **116**, 1 (1902)

Johnson and Peterson, *J. Am. Chem. Soc.*, **25**, 23

(1903, 1904)

When monochromatic light (i.e., light of a single frequency) is passed through a compound in the solution, one observes not only the incident beam but also several other frequencies which result from the characteristic atomic changes in the molecule. These changes are all directly related to the structure of the compound and are characteristic of which the following are typical:

1. Determination of structural formulae.
2. Determination of chemical groups.
3. Types of chemical groups: anti-parallel, parallel, etc.
4. Direction of chemical change.

THE RELATION BETWEEN ACIDITY AND TAUTOMERISM

F. Arndt and others,
Chemical Institute of
the University of Breslau.

Other Work: Use of diazomethane in synthesis.
Structure of Thiopyrones.

In 1932 F. Arndt and C. Martius studied the enotropic tendency (tendency to enolize) and the acidity of ketones carrying various substituents, and found these two qualities to be independent. The ability to confer acid properties by constituents is in the decreasing order:

SO_3R , SO_2R , SO_2NR_2 , CO_2R , CHO , COR , whereas the enotropic tendency for the last three substituents is in the decreasing order: CHO , COR , CO_2R . These results were obtained by use of the ferric chloride color reaction, bromine titration, and reaction with diazomethane.

The reaction of diazomethane was extended to study the relation between acidity and tautomerism in amides, hydroxamic acids, sulfinic acids, and sulfohydroxamic acids,² and in 1935 nitro compounds were investigated.³

The acidifying effect of the CN group when substituted on ketones was found to be stronger than that of any C-containing simple substituents and follows the SO_2R group in the list above.⁴ It was found that the $>\text{CHCN}$ group would be transformed into the enamide group if another group, such as CN, CO_2R , or NO_2 , is present on the same carbon. The $-\text{C}=\text{C}=\text{NH}$ group behaved toward FeCl_3 , Br_2 , and CH_2N_2 like the enol group.

1. Arndt and Martius, Ann., 499, 338 (1932).
2. Arndt and Scholz, Ann., 510, 62 (1934).
3. Arndt and Rose, J. Chem. Soc., 1-10 (1935).
4. Arndt, Scholz, and Frobel, Ann., 521, 95 (1935).

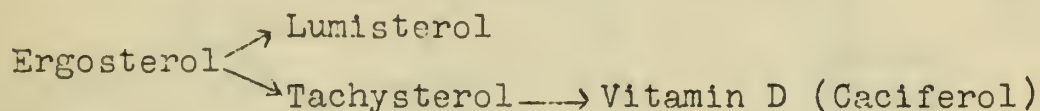
Reported by G. A. Nesty
March 11, 1936.

On the Constitution of Vitamin D₂

A. Windaus and W. Theile
Ann., 531, 160 (1935)
University Laboratories, Göttingen

Previous work: On the sterols, recently on
the irradiation of ergosterol.

The artificial irradiation of ergosterol leads to the following products:



Windaus has previously reported the isolation of Vitamin D from the irradiation products of ergosterol. This was described as Vitamin D₁, inasmuch as there were indications that a second antirachitic principle existed. Later it was found that D₁ was in reality the vitamin in combination with a physiologically inert isomer, lumisterol. Further purification resulted in the isolation of the vitamin, this being accomplished independently in the laboratories of Windaus and Askew. Askew used the term Calciferol for the vitamin, while Windaus designated it as Vitamin D₂.

The Vitamin D₂ obtained from the irradiation process is shown to have an empirical formula (C₂₈H₄₄O) identical with that of ergosterol. Thus it seems that the photochemical transformation must consist of a rearrangement of the double bonds or a steric transformation.

The vitamin is shown to possess four double bonds, in contrast to ergosterol which possesses only three, and hence it may contain only three rings.

Ozonization yields methyl iso-propyl aldehyde as does the ozonization of ergosterol. Hence the unsaturation in the side chain is between C₂₂ and C₂₃.

Maleic anhydride adds to the vitamin, which suggests the presence of a conjugated system. This addition is shown to take place between C₆ and C₁₈.

This vitamin-maleic acid addition product is reduced by the use of Pd and Hydrogen to the dihydro derivative in which the double bond between C₂₂ and C₂₃ is reduced.

Ozonization of this derivative yields the ketone C₁₉H₃₄O containing rings C and D.

A. Windaus and W. Pfeiffer
Ann., 1937, 197 (1937)
University of Bonn, Germany

Previous work: On the structure, recently on
the formation of ergosterol.

The structural investigation of ergosterol leads to the
following products:



Windaus has previously reported the isolation of Vitamin
D from the irradiation product of ergosterol. This was de-
scribed as Vitamin D₁. It was shown that there were indications that
a second antihypertensive principle existed. Later it was found
that D₁ was in reality the vitamin in combination with a
physiologically inert carrier, lanosterol. Further evidence
was obtained in the isolation of the vitamin, this being
accomplished independently by the investigators of Windaus
and Ashew. Ashew used the term Calciferol for the vitamin,
while Windaus described it as Vitamin D₂.

The Vitamin D₂ obtained from the irradiated precursor is
shown to have an empirical formula (C₂₈H₄₄O) identical with
that of ergosterol. Thus it seems that the photochemical
transformation must consist of a rearrangement of the double
bonds in a cyclic transformation.

The vitamin is shown to possess four double bonds, in
contrast to ergosterol which possesses only three, and hence
it may contain only three rings.

Isolation yields nearly 100% of the vitamin as does the
oxidation of ergosterol. Hence the transformation in the
chain is between C₂₈ and C₂₈.

Ultraviolet absorption data on the vitamin, which suggests the
presence of a conjugated system. This addition is shown by
tests made between C₂₈ and C₂₈.

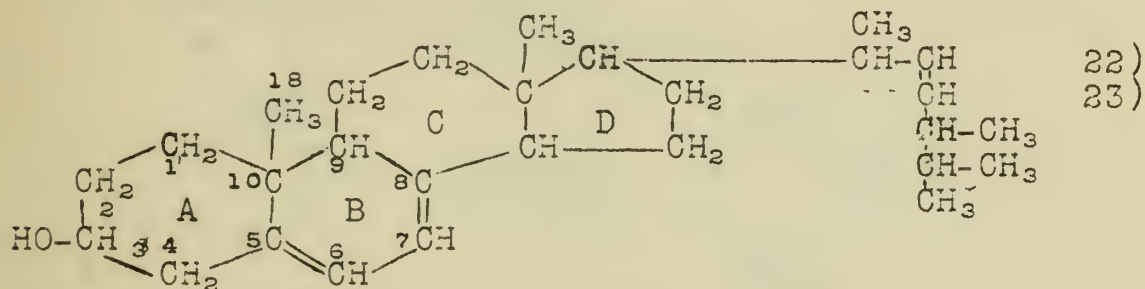
This vitamin-steroid acid addition product is reduced
by the use of H₂ and hydrogen to the dihydro-steroid in
which the double bond between C₂₈ and C₂₈ is reduced.

Constitution of this derivative yields the ketone (Vitamin)
containing rings D and E.

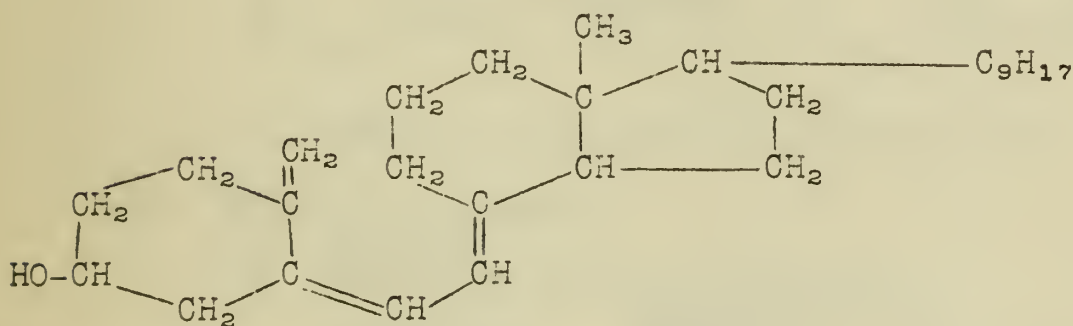
-2-

Treatment of the vitamin-maleic acid addition product with Pd yields naphthoic acid and naphthalene. Treatment with Se yields 2,3-dimethyl naphthalene. Thus it is concluded that a carboxyl-containing naphthalene ring is present in this derivative.

From these facts Windaus postulates the accompanying structure for Vitaming D₂.



Ergosterol

Vitamin D₂ (Calciferol)

Bibliography:

- Windaus, Ann., 489, 252 (1931)
 ibid., Ann., 492, 226 (1932)
 ibid., Ann., 499, 188 (1932)
 ibid., Ann., 521, 160 (1935)
 Lettre, Ann., 511, 285 (1934)
 Heilbron, Jour. Soc. Chem. Ind., 54, 795 (1935)
 Windaus, Angew. Chem., 48, 527 (1935).

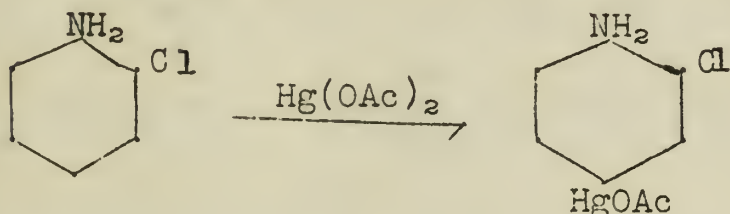
Reported by George B. Brown
 March 11, 1936.

Matejka, K., Ber., 69, 274 (1936)
 Carter, J. Biol. Chem., 112, 769 (1936)
 Wright, J. Am. Chem. Soc., 57, 1993 (1935)
 Abderhalden, Ber., 67, 530 (1934)
 Nails and Patet, J. Ind. Chem. Soc., 9, 185 (1932)
 and many others.

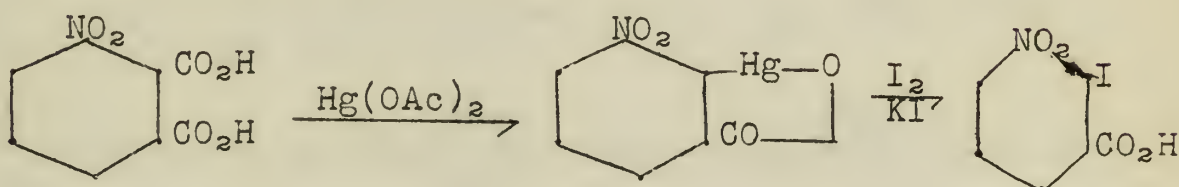
Previous work: Matejka -- none.

I. Substitution reactions

A. In an aromatic nucleus



B. Replacement reactions

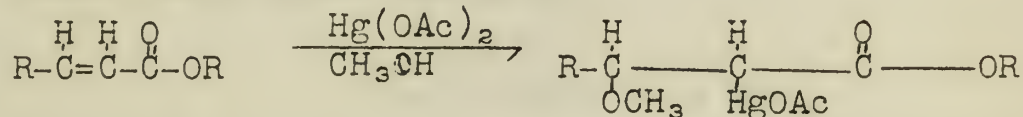


C. Effect of an active methylene group.

II. Addition reactions

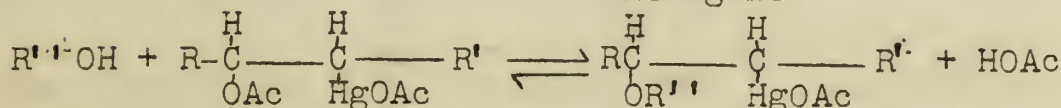
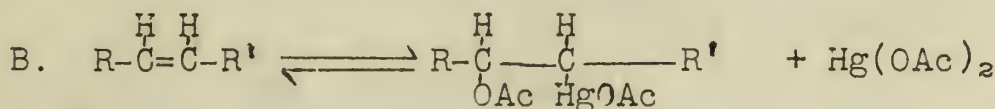
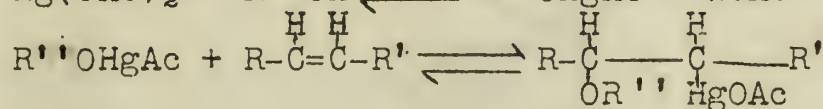
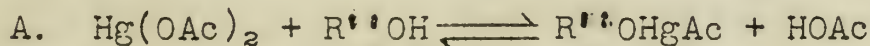
A. Olefins

B. Unsaturated acids and esters



C. Unsaturated phenols, phenolic ethers and coumarins.

III. Mechanism of addition reaction



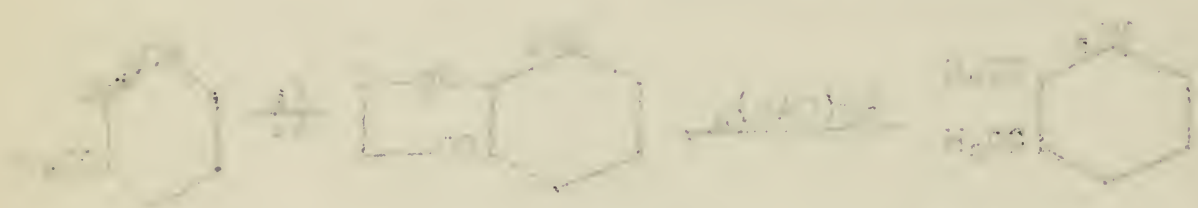
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 (5) $\frac{1}{6} \times 100 = 16.67$ (100% of 16.67)
 (6) $\frac{1}{7} \times 100 = 14.29$ (100% of 14.29)
 (7) $\frac{1}{8} \times 100 = 12.5$ (100% of 12.5)
 (8) $\frac{1}{9} \times 100 = 11.11$ (100% of 11.11)
 (9) $\frac{1}{10} \times 100 = 10$ (100% of 10)

(10) $\frac{1}{11} \times 100 = 9.09$ (100% of 9.09)
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 (18) $\frac{1}{19} \times 100 = 5.26$ (100% of 5.26)
 (19) $\frac{1}{20} \times 100 = 5$ (100% of 5)

(20) $\frac{1}{21} \times 100 = 4.76$ (100% of 4.76)
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 (24) $\frac{1}{25} \times 100 = 4$ (100% of 4)
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 (29) $\frac{1}{30} \times 100 = 3.33$ (100% of 3.33)

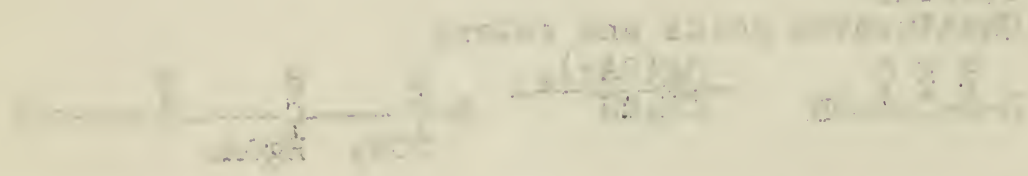


(40) $\frac{1}{41} \times 100 = 2.44$ (100% of 2.44)
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 (49) $\frac{1}{50} \times 100 = 2$ (100% of 2)



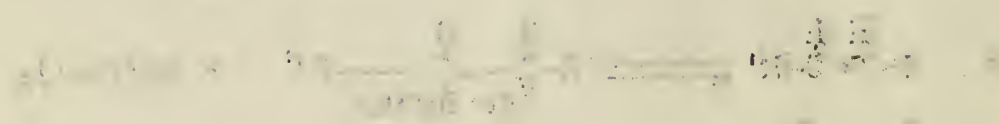
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 (79) $\frac{1}{80} \times 100 = 1.25$ (100% of 1.25)



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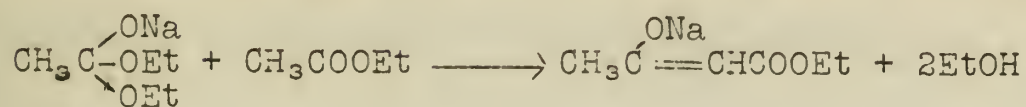
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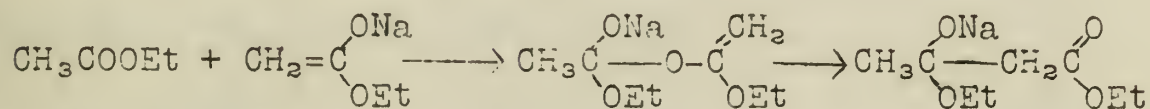
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THE MECHANISM OF THE ACETOACETICESTER CONDENSATION

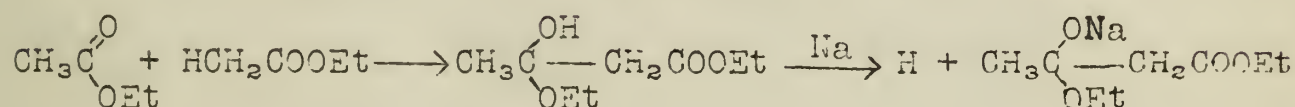
Claisen, Ber., 20, 652 (1887); Ann., 297, 92 (1897)



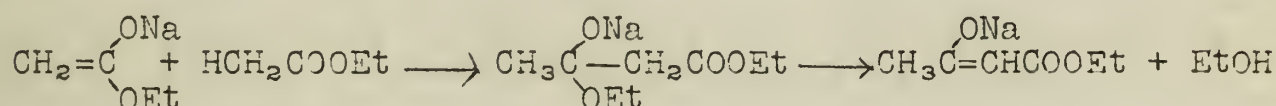
Claisen, Ber., 38, 709 (1905)



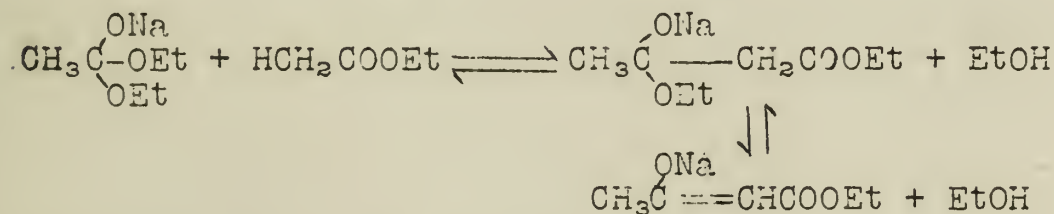
Michael, J. Prakt. Chem., (2) 37, 483 (1888)



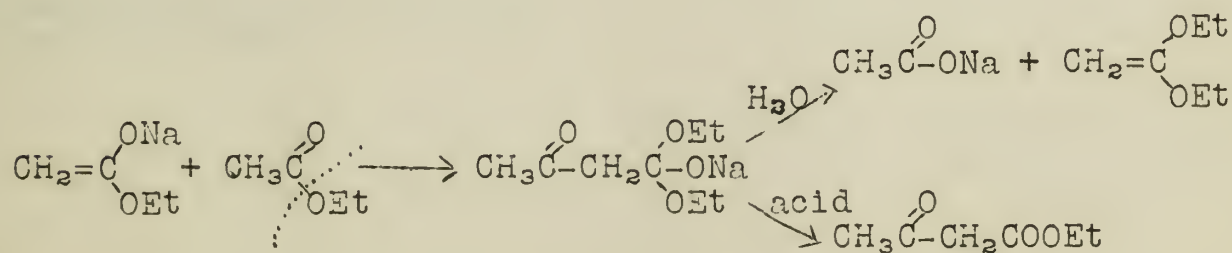
Nef, Ann., 298, 319 (1897); Michael, Ber., 38, 1922 (1905);
Schroeter, Ber., 49, 2706 (1916)



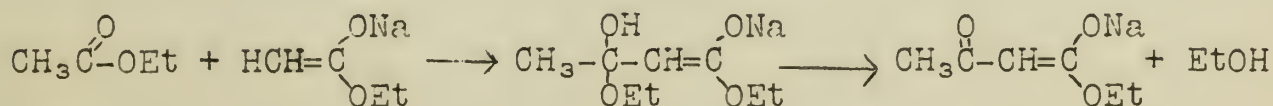
Dieckmann, Ber., 33, 2678 (1900)



Scheibler, Ber., 55, 789 (1922); 59, 1022 (1926)



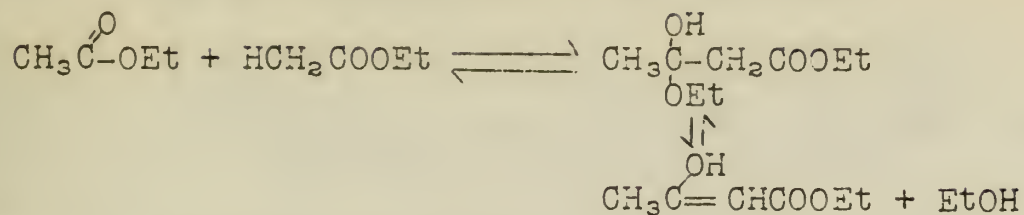
Chelintzev, Ber., 67B, 955-63 (1934)



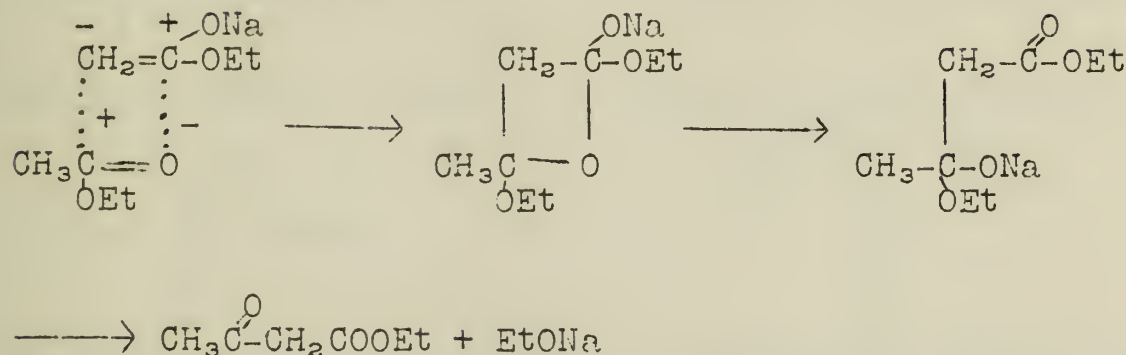
7. $\frac{1}{2} \times \frac{1}{2} = \frac{1}{4}$ (The probability of getting a head on the first toss and a head on the second toss is $\frac{1}{4}$.)

(1999) 100, 101, 104, 105, 106, 107, 108, 109, 110, 111, 112, 113, 114, 115, 116, 117, 118, 119, 120, 121, 122, 123, 124, 125, 126, 127, 128, 129, 130, 131, 132, 133, 134, 135, 136, 137, 138, 139, 140, 141, 142, 143, 144, 145, 146, 147, 148, 149, 150, 151, 152, 153, 154, 155, 156, 157, 158, 159, 160, 161, 162, 163, 164, 165, 166, 167, 168, 169, 170, 171, 172, 173, 174, 175, 176, 177, 178, 179, 180, 181, 182, 183, 184, 185, 186, 187, 188, 189, 190, 191, 192, 193, 194, 195, 196, 197, 198, 199, 200, 201, 202, 203, 204, 205, 206, 207, 208, 209, 210, 211, 212, 213, 214, 215, 216, 217, 218, 219, 220, 221, 222, 223, 224, 225, 226, 227, 228, 229, 230, 231, 232, 233, 234, 235, 236, 237, 238, 239, 240, 241, 242, 243, 244, 245, 246, 247, 248, 249, 250, 251, 252, 253, 254, 255, 256, 257, 258, 259, 260, 261, 262, 263, 264, 265, 266, 267, 268, 269, 270, 271, 272, 273, 274, 275, 276, 277, 278, 279, 280, 281, 282, 283, 284, 285, 286, 287, 288, 289, 290, 291, 292, 293, 294, 295, 296, 297, 298, 299, 300, 301, 302, 303, 304, 305, 306, 307, 308, 309, 310, 311, 312, 313, 314, 315, 316, 317, 318, 319, 320, 321, 322, 323, 324, 325, 326, 327, 328, 329, 330, 331, 332, 333, 334, 335, 336, 337, 338, 339, 340, 341, 342, 343, 344, 345, 346, 347, 348, 349, 350, 351, 352, 353, 354, 355, 356, 357, 358, 359, 360, 361, 362, 363, 364, 365, 366, 367, 368, 369, 370, 371, 372, 373, 374, 375, 376, 377, 378, 379, 380, 381, 382, 383, 384, 385, 386, 387, 388, 389, 390, 391, 392, 393, 394, 395, 396, 397, 398, 399, 400, 401, 402, 403, 404, 405, 406, 407, 408, 409, 410, 411, 412, 413, 414, 415, 416, 417, 418, 419, 420, 421, 422, 423, 424, 425, 426, 427, 428, 429, 430, 431, 432, 433, 434, 435, 436, 437, 438, 439, 440, 441, 442, 443, 444, 445, 446, 447, 448, 449, 450, 451, 452, 453, 454, 455, 456, 457, 458, 459, 460, 461, 462, 463, 464, 465, 466, 467, 468, 469, 470, 471, 472, 473, 474, 475, 476, 477, 478, 479, 480, 481, 482, 483, 484, 485, 486, 487, 488, 489, 490, 491, 492, 493, 494, 495, 496, 497, 498, 499, 500, 501, 502, 503, 504, 505, 506, 507, 508, 509, 510, 511, 512, 513, 514, 515, 516, 517, 518, 519, 520, 521, 522, 523, 524, 525, 526, 527, 528, 529, 530, 531, 532, 533, 534, 535, 536, 537, 538, 539, 540, 541, 542, 543, 544, 545, 546, 547, 548, 549, 550, 551, 552, 553, 554, 555, 556, 557, 558, 559, 560, 561, 562, 563, 564, 565, 566, 567, 568, 569, 570, 571, 572, 573, 574, 575, 576, 577, 578, 579, 580, 581, 582, 583, 584, 585, 586, 587, 588, 589, 590, 591, 592, 593, 594, 595, 596, 597, 598, 599, 600, 601, 602, 603, 604, 605, 606, 607, 608, 609, 610, 611, 612, 613, 614, 615, 616, 617, 618, 619, 620, 621, 622, 623, 624, 625, 626, 627, 628, 629, 630, 631, 632, 633, 634, 635, 636, 637, 638, 639, 640, 641, 642, 643, 644, 645, 646, 647, 648, 649, 650, 651, 652, 653, 654, 655, 656, 657, 658, 659, 660, 661, 662, 663, 664, 665, 666, 667, 668, 669, 670, 671, 672, 673, 674, 675, 676, 677, 678, 679, 680, 681, 682, 683, 684, 685, 686, 687, 688, 689, 690, 691, 692, 693, 694, 695, 696, 697, 698, 699, 700, 701, 702, 703, 704, 705, 706, 707, 708, 709, 710, 711, 712, 713, 714, 715, 716, 717, 718, 719, 720, 721, 722, 723, 724, 725, 726, 727, 728, 729, 730, 731, 732, 733, 734, 735, 736, 737, 738, 739, 740, 741, 742, 743, 744, 745, 746, 747, 748, 749, 750, 751, 752, 753, 754, 755, 756, 757, 758, 759, 760, 761, 762, 763, 764, 765, 766, 767, 768, 769, 770, 771, 772, 773, 774, 775, 776, 777, 778, 779, 780, 781, 782, 783, 784, 785, 786, 787, 788, 789, 790, 791, 792, 793, 794, 795, 796, 797, 798, 799, 800, 801, 802, 803, 804, 805, 806, 807, 808, 809, 810, 811, 812, 813, 814, 815, 816, 817, 818, 819, 820, 821, 822, 823, 824, 825, 826, 827, 828, 829, 830, 831, 832, 833, 834, 835, 836, 837, 838, 839, 840, 841, 842, 843, 844, 845, 846, 847, 848, 849, 850, 851, 852, 853, 854, 855, 856, 857, 858, 859, 860, 861, 862, 863, 864, 865, 866, 867, 868, 869, 870, 871, 872, 873, 874, 875, 876, 877, 878, 879, 880, 881, 882, 883, 884, 885, 886, 887, 888, 889, 890, 891, 892, 893, 894, 895, 896, 897, 898, 899, 900, 901, 902, 903, 904, 905, 906, 907, 908, 909, 910, 911, 912, 913, 914, 915, 916, 917, 918, 919

McElvain, J. Am. Chem. Soc., 56, 1173 (1934)



Bodendorf, Ber., 67B, 1338 (1934)



In the most recent work on the mechanism of this reaction, Adickes and Meister, Ber., 68, 2191 (1935), have obtained evidence indicating the mechanisms of Claisen and Scheibler to be incorrect. This work was done at the Chemical Institute of Tübingen University.

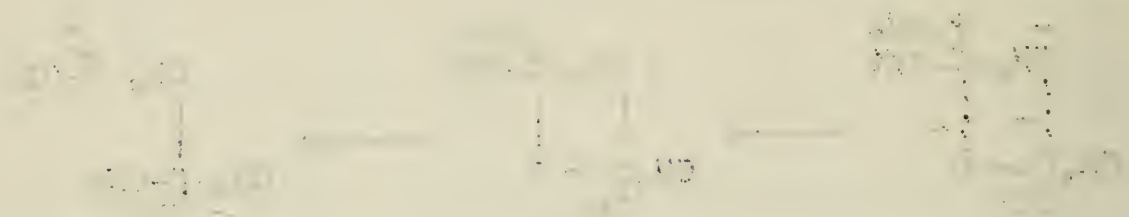
Reported by P. S. Pinkney
March 18, 1936

(1991) 177 (2) 100-101

100-101 (2) 100-101

100-101 (2) 100-101

100-101 (2) 100-101



100-101 (2) 100-101

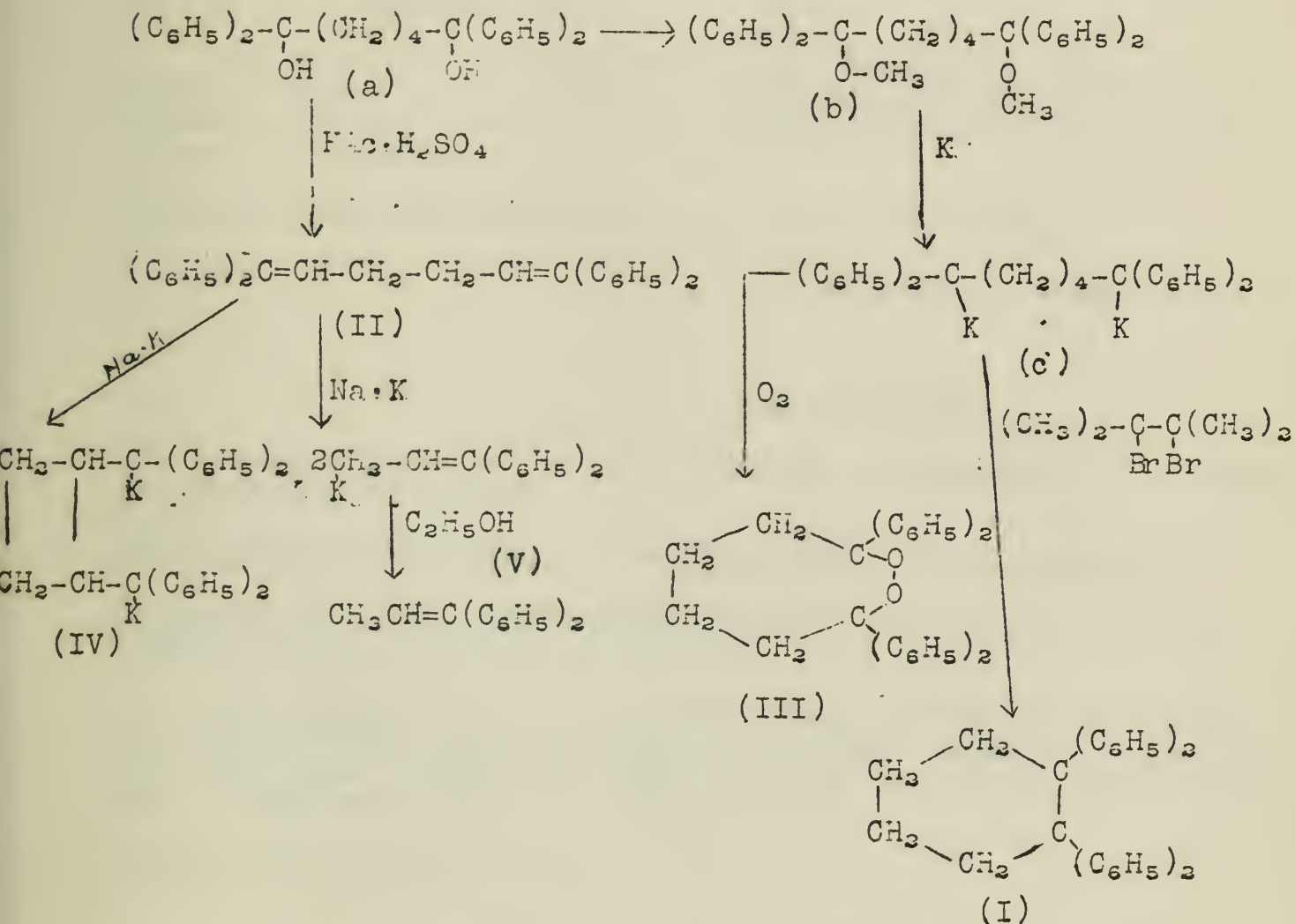
100-101 (2) 100-101

100-101 (2) 100-101

Some Researches on the Effect of
Tetra (*E*,*β*-Diphenylvinyl) Substitution
on the Strength of the Ethane Band.

G. Wittig and Leo, Ber., 63, 943 (1930)
G. Wittig Ber., 64, 437 (1931)
G. Wittig and Obermann, Ber., 68, 2214 (1935)
Marbourg -- Chemical Institute

In an investigation on the effect of a ring structure on free radical formation Wittig *et al* attempted to prepare 1,1,2,2-tetraphenylcyclohexane by the following series of reactions:
(a) \longrightarrow (b) \longrightarrow (c) \longrightarrow (I)



The cyclohexane (I) was not obtained, instead a mixture of unknown composition resulted. However, a peroxide which analyzed for (III) could be obtained.

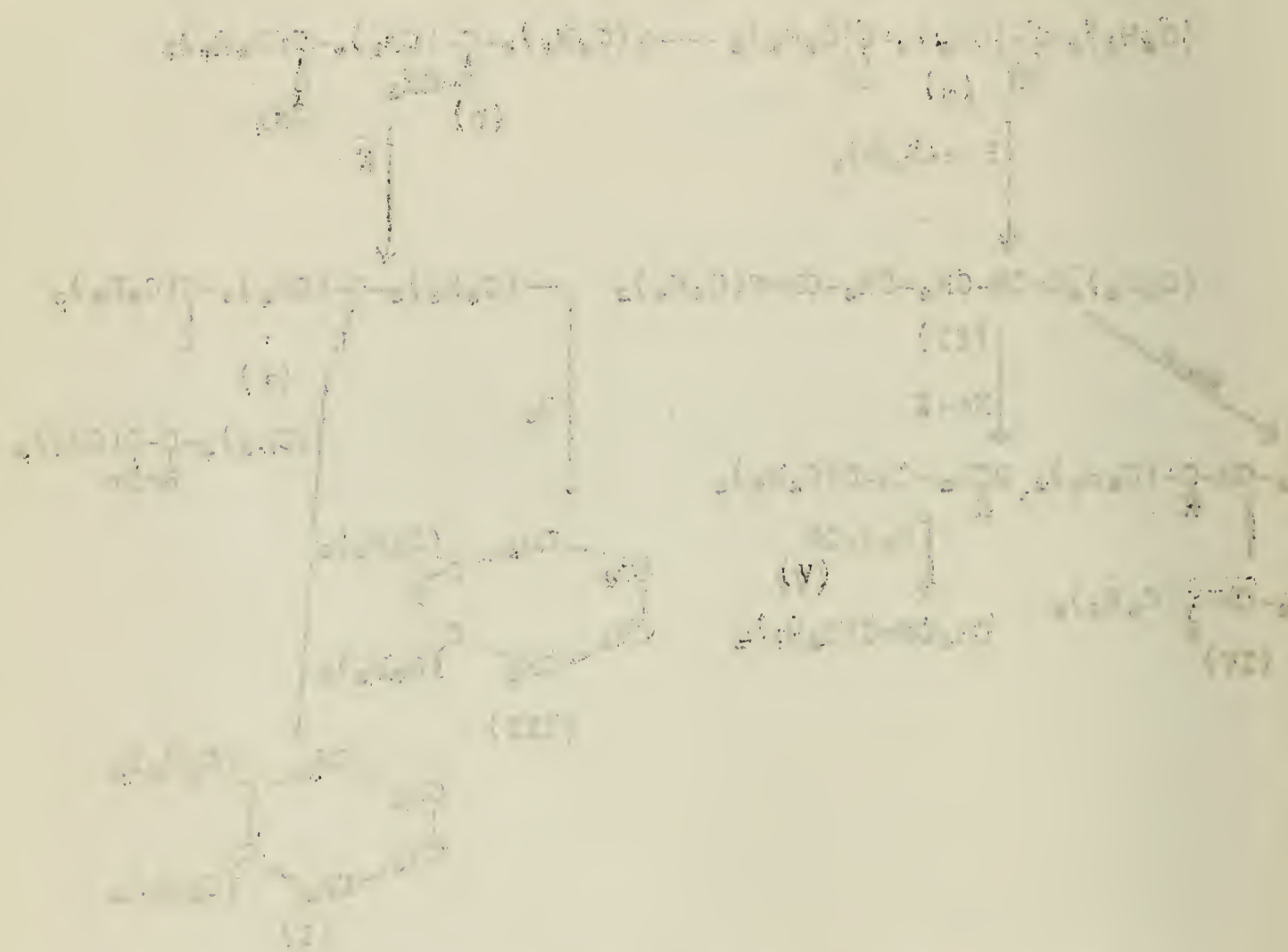
Treatment of the dipotassium compound (c) with alcohol formed 1,1,6,6-tetraphenylhexane.

It was thought that treatment of 1,1,6,6-tetraphenylhexadiene 1,5 (II) by Na · K alloy would give the cyclobutane (IV). Actually the K compound (V) was obtained and treatment with alcohol gave 1,1-diphenylpropene-1.

THE UNIVERSITY OF CHICAGO
 DEPARTMENT OF CHEMISTRY
 5700 S. DICKINSON AVE., CHICAGO, ILL. 60637

REPORT OF THE RESEARCH GROUP ON
 THE CHEMISTRY OF THE
 CARBON-13 ISOTOPE
 (1961-1962)

THIS REPORT IS A SUMMARY OF THE RESEARCH WORK OF THE
 RESEARCH GROUP ON THE CHEMISTRY OF THE CARBON-13 ISOTOPE
 DURING THE YEAR 1961-1962. THE RESEARCH WAS SUPPORTED BY
 THE NATIONAL SCIENCE FOUNDATION.

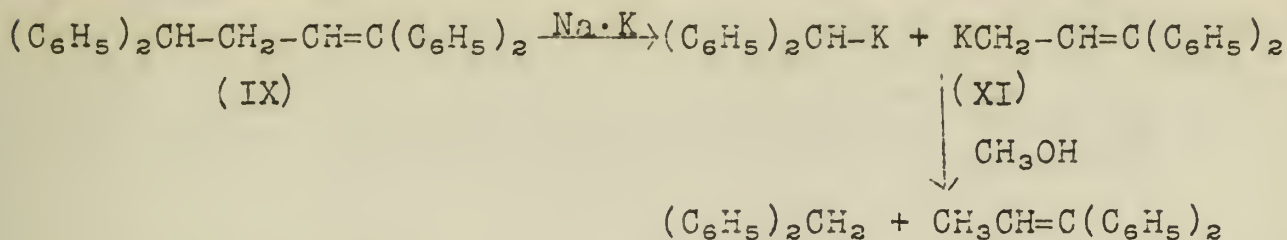


THE RESEARCH WAS SUPPORTED BY THE NATIONAL SCIENCE FOUNDATION
 UNDER A GRANT TO THE UNIVERSITY OF CHICAGO.

REPORT OF THE RESEARCH GROUP ON THE CHEMISTRY OF THE
 CARBON-13 ISOTOPE

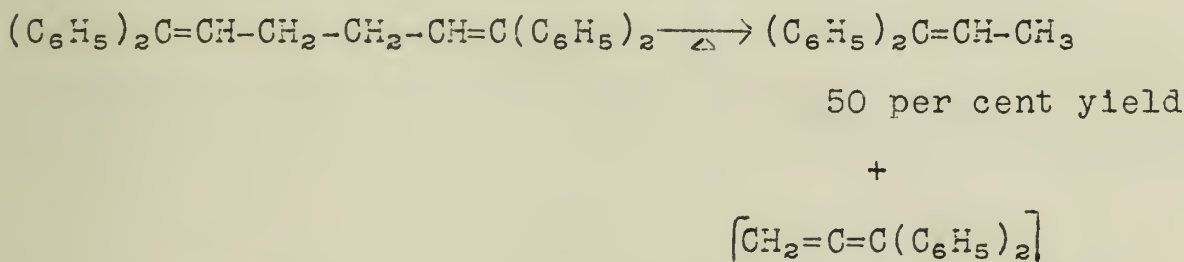
THE RESEARCH WAS SUPPORTED BY THE NATIONAL SCIENCE FOUNDATION
 UNDER A GRANT TO THE UNIVERSITY OF CHICAGO.

Further evidence of the splitting of the ethane band by an alkali metal was obtained by the following series of reactions:

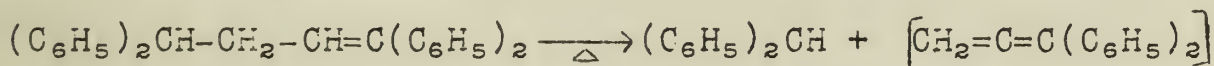


Thus the ethane band is weakened by certain groups and the effect of such groups on this band is evidently transferred through the linkage $-\text{C}=\text{C}-$.

The weakness of the band is also observed in thermal decomposition. 1,1,6,6-Tetraphenylhexadiene-1,5 (II) can be vacuum distilled indecomposed, but distillation at atmospheric pressure causes disproportionation.

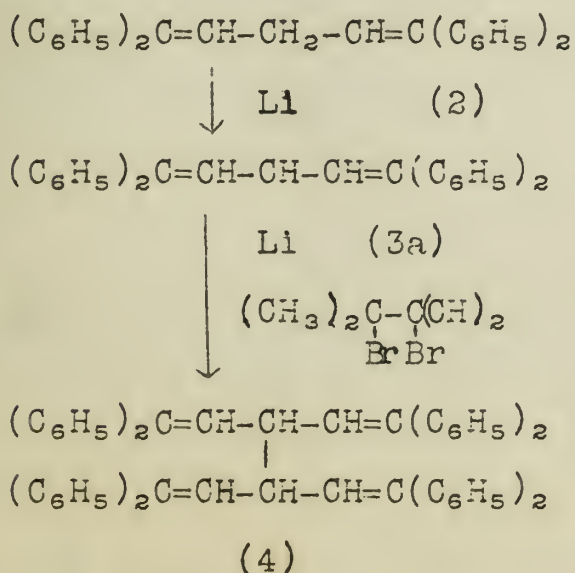


1,1,4,4-Tetraphenylbutene-1 is likewise decomposed on distilling at atmospheric pressure.



In contrast, 1,1,4,4-tetraphenylbutene 2 can be distilled indecomposed at atmospheric pressure.

This effect of a β,β -diphenyl group led Wittig to attempt to prepare tetra- $(\beta,\beta$ -diphenylvinyl)-ethane, with the expectation that such a compound might manifest some free radical tendency. This was done as follows:



Further evidence of the existence of the above said is an
abstract of the same, which is attached to the present
document. The same is a copy of the original, and is
correctly stated.

THE ABOVE SAID IS A COPY OF THE ORIGINAL

And the evidence of the same is as follows: The above
said is a copy of the original, and is correctly stated.

The evidence of the same is as follows: The above
said is a copy of the original, and is correctly stated.

THE ABOVE SAID IS A COPY OF THE ORIGINAL

AND THE EVIDENCE OF THE SAME IS AS FOLLOWS:

THE ABOVE SAID IS A COPY OF THE ORIGINAL

And the evidence of the same is as follows: The above
said is a copy of the original, and is correctly stated.

THE ABOVE SAID IS A COPY OF THE ORIGINAL

AND THE EVIDENCE OF THE SAME IS AS FOLLOWS:

The evidence of the same is as follows: The above
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(4) is a colorless solid m.p. 169-175°. It dissolves in zylene to give a colorless solution. By heating the solution to boiling a yellow color develops; on cooling the color disappears. This can be repeated many times. However, on prolonged boiling the solution remains colored and the original material can not be recovered. This may be interpreted that (4) dissociates at high temperatures.

Reported by G. E. Ulliot
March 25, 1936.

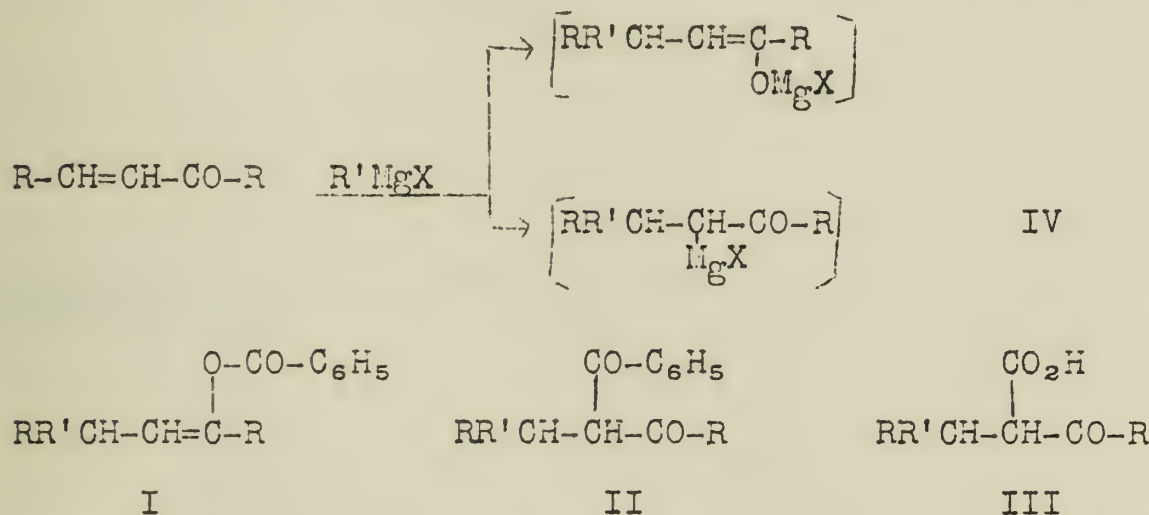
The Structure of the Metallic Derivatives
which are Formed by Adding Grignard Reagents
to Unsaturated Ketones

Kohler and Tischler, J. Am. Chem. Soc., 54, 1594 (1932)
Kohler, Tischler and Potter, J. Am. Chem. Soc., 57,
2517 (1935).

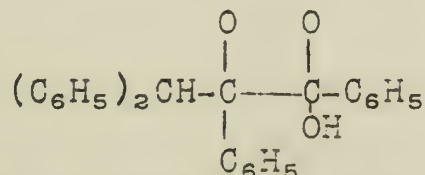
, Harvard University

Kohler, in 1905, had suggested that the primary addition of a Grignard reagent to an α,β -unsaturated ketone was 1,4 to the conjugated system. On treatment of the metallic addition compound with benzoyl chloride he obtained a substance which he thought to be the benzoate I, but which he subsequently found to be the β -diketone II.

Because of the formation of the β -diketone on benzylation, and because a β -keto acid III was formed when the metallic derivative was treated with carbon dioxide, Umnowa postulated the intermediate formation of a carbon-magnesium complex IV.



The first evidence that the addition was 1,4 was obtained when Kohler and Kischler treated an α,β -unsaturated ketone which contained an aryl group in the α position with the Grignard reagent, and obtained, on hydrolysis of the addition compound, an enolic substance stable enough to form a peroxide.



The magnesium derivatives of β,β -diphenylpropionylmesitylene may be obtained by three methods. Treatment of a substance obtained by one of these methods with benzoyl chloride gives a different compound than is isolated when the magnesium derivative prepared by the other two methods is so treated. Ease of hydrolysis indicates that the two substances are the benzoates, V and its geometric isomer.

THE SECRETARY OF THE ARMY
WASHINGTON, D. C.
JAN 10 1918

TO THE SECRETARY OF THE ARMY
FROM THE SECRETARY OF THE ARMY
SUBJECT: [illegible]

[illegible text]

[illegible text]

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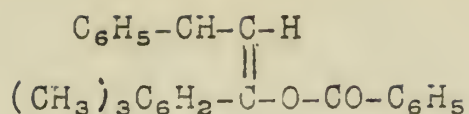
[illegible text]

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-2-



v

Isolation of these two isomers proves that the addition of the Grignard reagent to a conjugated system $\text{C}=\text{C}-\text{C}=\text{O}$ gives rise to an $-\text{OMgX}$ linkage.

The enol which is obtained on hydrolysis of the isomers has remarkable stability. It appears to be completely permanent in the solid form, and can be recrystallized without change. The unusual lack of mobility in this enol, doubtless is largely due to the mesityl group, for if the mesitylene nucleus is replaced by phenyl the mobility becomes normal.

Reported by Harry H. Weinstock, Jr.
March 25, 1936.

REPORT OF THE COMMISSIONER OF THE LAND OFFICE

The following is a list of the lands owned by the State of New York, as of the 1st of January, 1890. The lands are classified according to their location, and the amount of land in each class is given in acres. The total amount of land owned by the State is 1,000,000 acres.

The lands are classified as follows:

- 1. Lands in the State of New York, as of the 1st of January, 1890.
- 2. Lands in the State of New York, as of the 1st of January, 1890.
- 3. Lands in the State of New York, as of the 1st of January, 1890.
- 4. Lands in the State of New York, as of the 1st of January, 1890.
- 5. Lands in the State of New York, as of the 1st of January, 1890.
- 6. Lands in the State of New York, as of the 1st of January, 1890.
- 7. Lands in the State of New York, as of the 1st of January, 1890.
- 8. Lands in the State of New York, as of the 1st of January, 1890.
- 9. Lands in the State of New York, as of the 1st of January, 1890.
- 10. Lands in the State of New York, as of the 1st of January, 1890.

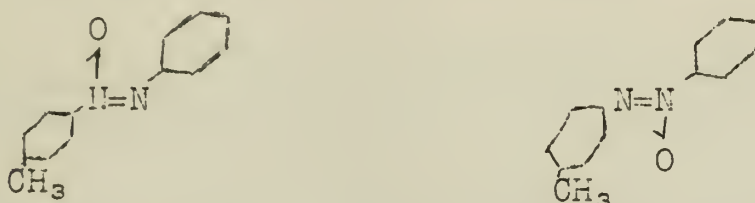
REPORT OF THE
COMMISSIONER OF THE
LAND OFFICE

Bigelow, Chem. Rev., 9, 117 (1931)
 Chu and Marvel, J. Am. Chem. Soc., 55, 2841 (1933)
 Muller, Ann., 493, 166 (1932)
 Muller, Ann., 495, 132 (1932)
 Muller and Hory, Z. Physik. Chem., 162, 281 (1932)
 Gerckens and Muller, Ann., 500, 296 (1933)
 Muller and Illgen, Ann., 521, 73 (1935)

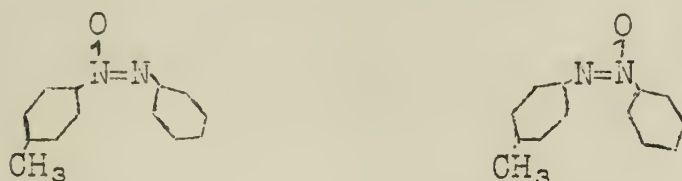
Location: Muller--Technische Hochschule Danzig-Langfuhr.

I. Isomerism.

Structural isomerism permits an azoxybenzene of the type ArN_2OAr' to exist in the two stable trans forms:

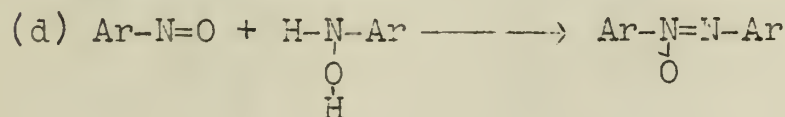
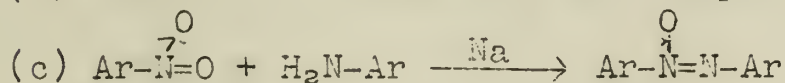


The cis isomers of some azoxybenzenes are also known giving the additional labile forms:



II. Methods of preparation.

- (a) Reduction of nitro compounds
- (b) Oxidation of amines or azo compounds



III. Reactions.

- (a) Oxidation and reduction
- (b) Substitution (the tervalent nitrogen enhances the activity of the ring to which it is attached)
- (c) Wallach's rearrangement.

Reported by William Fessler
 April 1, 1936.

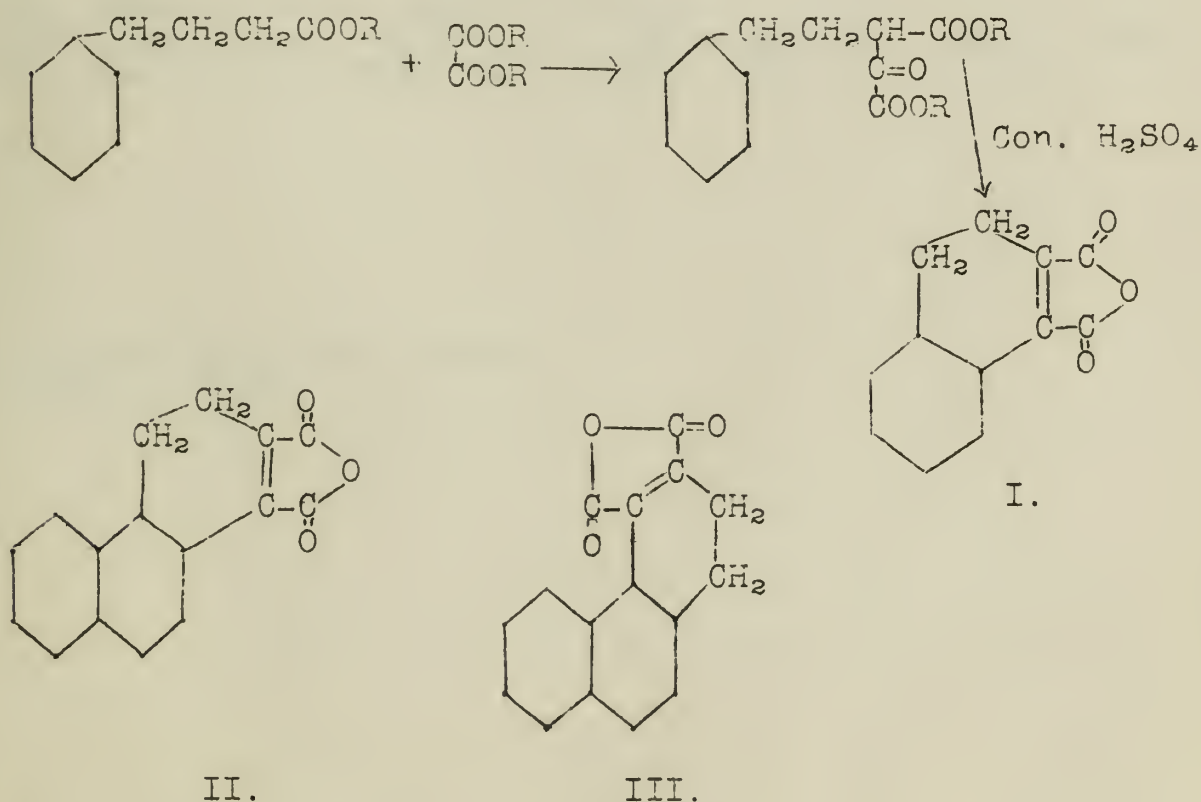
Harvard University.

1. Pschorr's - developed for application to studies in the morphine series, it utilized o-nitrobenzaldehyde and phenyl acetic acid.¹

2. Bardhan and Sengupta's - was first applied in studies on resin acids, it employed a cyclic beta-keto-ester and a substituted beta-phenyl ethyl bromide.²

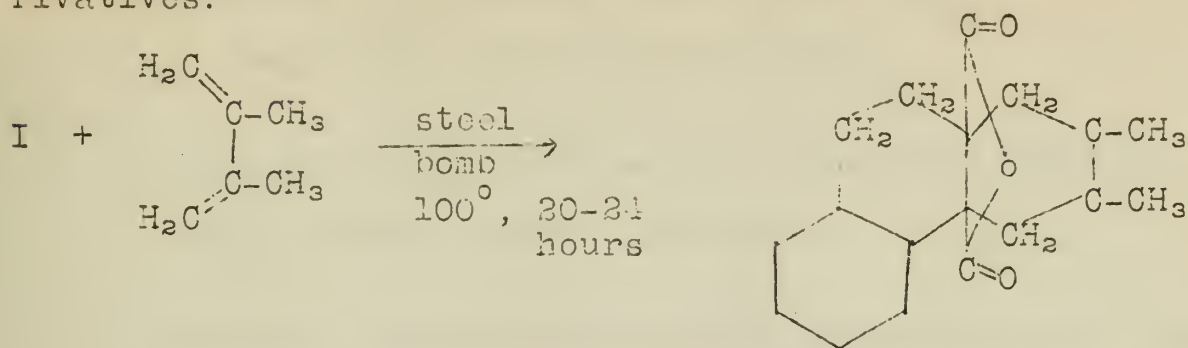
3. Cyclization of gamma-aryl butyric acids - used in studies on sterols and related substances.

Fieser and Hershberg have used gamma-aryl butyric esters in the Bougault reaction as shown:



II and III have also been prepared.

These anhydrides are used in a new "Hydrocarbon Synthesis" for phenanthrene and hydrophenanthrene derivatives:



IV.

From IV there have been prepared the dibasic acid, the acid and the neutral esters, the reduced anhydride and the corresponding substituted aromatic hydrocarbon.

Further studies of the diene addition products and further applications of this new phenanthrene synthesis are in progress.

1. Pschorr, Ber., 29, 496 (1896).
2. Bardhan and Sengupta, J. Chem. Soc., 1932, 2530, 2798.
3. Haworth, J. Chem. Soc., 1932, 1125.

Reported by Allene Jeanes
April 1, 1936.

Oxidation of Olefinic Double Bonds with
Perbenzoic and Peracetic Acids

From the work of Prilezhaev, Böeseken, Meerwein,
Smit, Braun, Muskat, and others.

In 1909 Prilezhaev reported that perbenzoic acid would oxidize olefinic double bonds to give the cyclic oxide which in most cases could be hydrolyzed to the corresponding glycol. Since then much work has been done in this field so that it is now possible to use this acid and peracetic acid to quantitatively determine certain double bonds.

Ordinarily conjugated systems do not react normally, and α,β -unsaturated carbonyls are especially inert to oxidation. However, the following observations have been made regarding isolated olefinic double bond oxidation:

1. The more highly alkylated the olefin, the greater will be the speed of oxidation.
2. With aryl compounds, the nearer the double bond to the aromatic nucleus, the greater will be the speed of oxidation.
3. With aliphatic compounds, RCOO and OH are added trans to the double bond.

Reported by Wm. E. Lundquist

April 8, 1936.

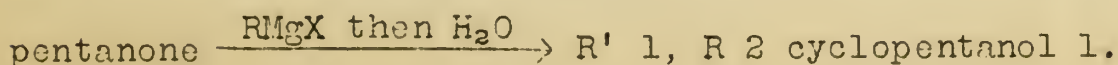
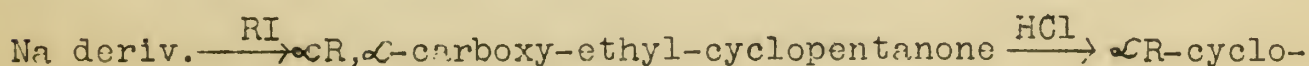
CIS-TRANS ISOMERISM IN SUBSTITUTED CYCLOPENTANOLS

- G. Chiurdoglu, Bul. Soc. Chim. Belg., 44, 523 (1935)
 G. Vavon, Bul. Soc. Chim. France, 49, 989 (1931)
 W. Huckel, L. Annalen, 477, 154 (1930)

Some of the methods used in assigning structures to a pair of these geometric isomers are:

- and platinum
- I. Methods of preparation.--Reduction with hydrogen/in acid solution gives a preponderance of the cis isomer; while in neutral solution or with sodium and alcohol a preponderance of the trans isomer is formed in the reduction of substituted phenols, toluidides, cyclopentanones, etc.
- II. Correlation of physical data on the two isomers.--Auwers' rule states that in a pair of cis-trans cyclanes the cis form has the greater density and index of refraction, and the smaller molecular refraction. This has been found generally true in cyclohexanes and cyclopentanes, but exceptions exist.
 Stoermer found that in 19 cis-trans isomers containing the group $-\text{CO}_2\text{CH}_3$ the trans isomer had the higher boiling point in every case.
- III. Chemical reactions of the two isomers.--In cyclopentanes containing an OH or NH_2 group, and a $-\text{COOH}$ group, the formation of a lactone or lactam indicates a cis structure.
 In a pair of substituted cyclopentanol the isomer dehydrating the most readily is the one where the OH is in a trans position with the H with which it is eliminated.
 In a pair of substituted cyclopentanol the trans isomer will esterify faster than the cis, and the corresponding trans ester will saponify faster than the cis.
 In the special case of cyclopentane-diols 1,2 the cis isomer gives a higher augmentation to the conductivity of boric acid solutions, reacts with acetone and HCl to form an acetal, and is split faster by lead acetate.

A new method of distinguishing the cis and trans isomers in dialkyl-1,2-cyclopentanol-1 has recently been developed by G. Chiurdoglu. Most of the above methods require the comparison of the two isomers before either can be assigned a structure. The new method permits the identification of one of these pentanols when its isomer is not available. He prepared dimethyl-1,2-methyl-1-propyl-2, methyl-1-ethyl-2, and diethyl-1,2-cyclopentanol-1 by the following reactions:



These were separated by fractional distillation into the cis and trans isomers, with the exception of the diethyl-1,2-cyclopentanol-1, which could not be separated. Structures were assigned to these isomers by using physical data and the rule of transelimination of water. The rate of adsorption of hydrogen by these pentanols in the presence of platinum black was measured. Under comparable conditions all cis isomers react at the same rate, and all trans isomers at a faster but common rate. This enables one to definitely assign the trans structure to the diethyl cyclopentanol. In this reaction the product formed from either the cis or the trans cyclopentanol is identical, being about 80 per cent trans dialkyl-1,2-cyclopentane. The unreacted alcohol is unchanged in structure. The reaction does not go through the olefin. As in dehydration the rate of reaction is greatest when the tertiary OH and H are in a trans position with respect to each other.

Reported by K. Kearby
April 8, 1936.

W. O. Lukaschewitsch, Ann., 521, 198 (1936)

Place: Forschungsinstitut für organische Zwischen-
produkte und Farbstoffe, Moskau.

Previous work:

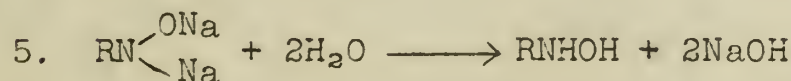
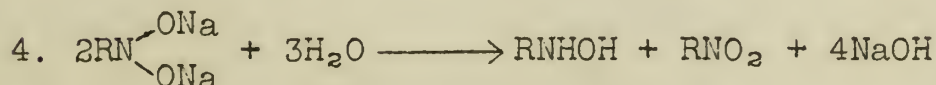
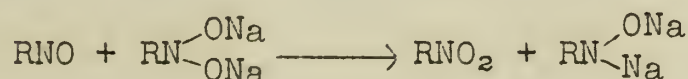
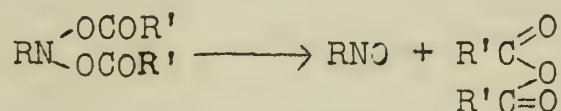
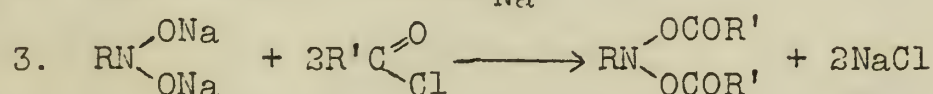
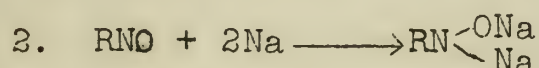
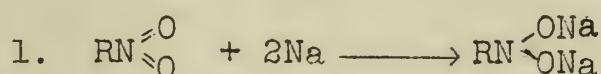
When 0.5 per cent sodium amalgam is allowed to react with aromatic nitro and nitroso compounds under an atmosphere of nitrogen, compounds containing sodium are formed.

In order to ascertain their structures these compounds were allowed to react with benzoyl chloride and with water.

The reaction of benzoyl chloride with the sodium derivatives of the nitro and nitroso compounds yielded α , β -dibenzoyl aryl hydroxyl amines.

The action of water on the sodium derivatives gave rise to β -aryl hydroxyl amines.

The equations for the formation of the derivatives and their reactions are:



References:

- Ber., 5, 915 (1872)
Ber., 30, 1572 (1897)
Ber., 32, 2911 (1899)
Ber., 32, 2919 (1899)

Reported by W. E. Ross
April 15, 1936.

PROBLEM SET 10

Let R be a Dedekind domain. For each prime ideal \mathfrak{p} of R , let $\pi_{\mathfrak{p}}$ be a uniformizer of $R_{\mathfrak{p}}$. Let $f_{\mathfrak{p}}$ be the inertia degree of \mathfrak{p} over \mathbb{Q} . Let N be a positive integer. Let S_N be the set of prime ideals \mathfrak{p} of R such that $\mathfrak{p} \mid N$.

1. Let \mathfrak{p} be a prime ideal of R . Let $\pi_{\mathfrak{p}}$ be a uniformizer of $R_{\mathfrak{p}}$. Let $f_{\mathfrak{p}}$ be the inertia degree of \mathfrak{p} over \mathbb{Q} . Let N be a positive integer. Let S_N be the set of prime ideals \mathfrak{p} of R such that $\mathfrak{p} \mid N$.

2. Let \mathfrak{p} be a prime ideal of R . Let $\pi_{\mathfrak{p}}$ be a uniformizer of $R_{\mathfrak{p}}$. Let $f_{\mathfrak{p}}$ be the inertia degree of \mathfrak{p} over \mathbb{Q} . Let N be a positive integer. Let S_N be the set of prime ideals \mathfrak{p} of R such that $\mathfrak{p} \mid N$.

3. Let \mathfrak{p} be a prime ideal of R . Let $\pi_{\mathfrak{p}}$ be a uniformizer of $R_{\mathfrak{p}}$. Let $f_{\mathfrak{p}}$ be the inertia degree of \mathfrak{p} over \mathbb{Q} . Let N be a positive integer. Let S_N be the set of prime ideals \mathfrak{p} of R such that $\mathfrak{p} \mid N$.

4. Let \mathfrak{p} be a prime ideal of R . Let $\pi_{\mathfrak{p}}$ be a uniformizer of $R_{\mathfrak{p}}$. Let $f_{\mathfrak{p}}$ be the inertia degree of \mathfrak{p} over \mathbb{Q} . Let N be a positive integer. Let S_N be the set of prime ideals \mathfrak{p} of R such that $\mathfrak{p} \mid N$.

$$1. \quad \pi_{\mathfrak{p}}^{f_{\mathfrak{p}}} \mid N$$

$$2. \quad \pi_{\mathfrak{p}}^{f_{\mathfrak{p}}} \mid N$$

$$3. \quad \pi_{\mathfrak{p}}^{f_{\mathfrak{p}}} \mid N$$

$$4. \quad \pi_{\mathfrak{p}}^{f_{\mathfrak{p}}} \mid N$$

$$5. \quad \pi_{\mathfrak{p}}^{f_{\mathfrak{p}}} \mid N$$

$$6. \quad \pi_{\mathfrak{p}}^{f_{\mathfrak{p}}} \mid N$$

$$7. \quad \pi_{\mathfrak{p}}^{f_{\mathfrak{p}}} \mid N$$

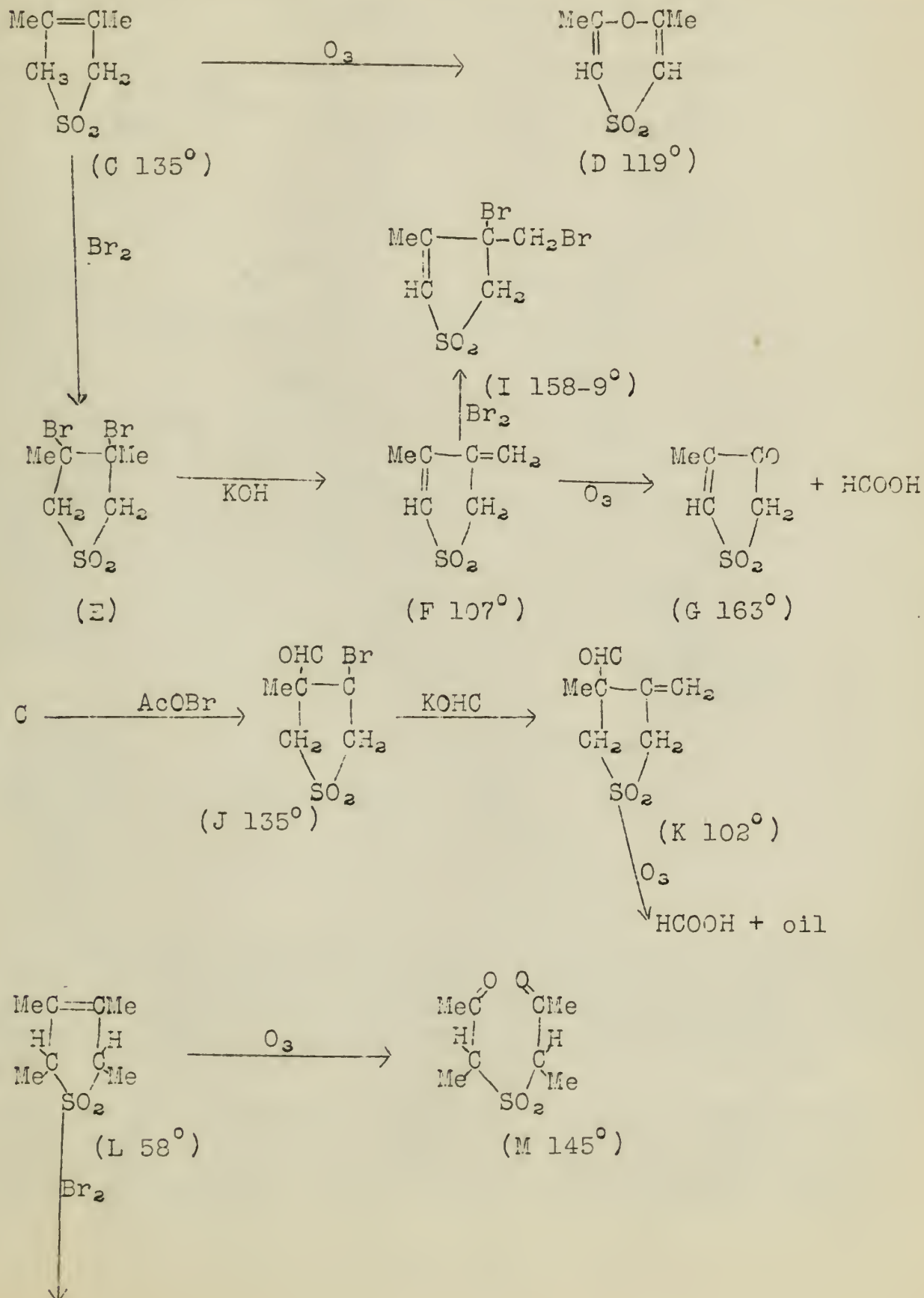
$$8. \quad \pi_{\mathfrak{p}}^{f_{\mathfrak{p}}} \mid N$$

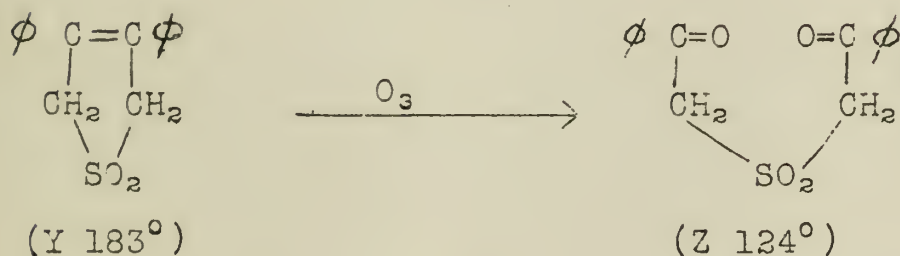
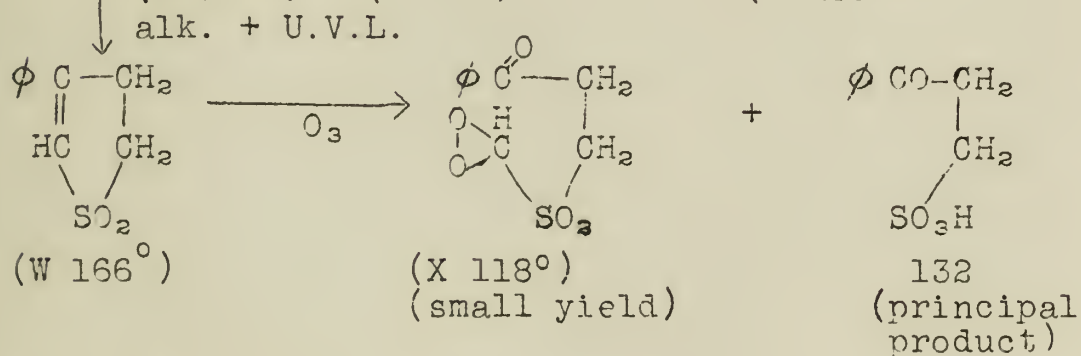
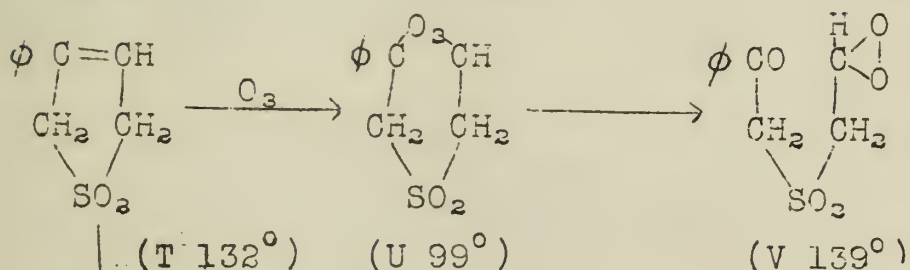
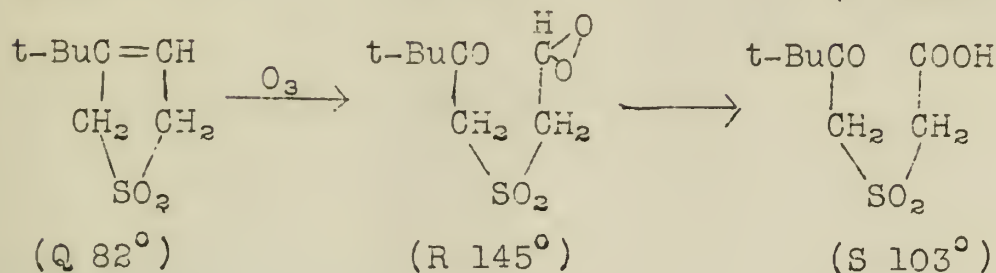
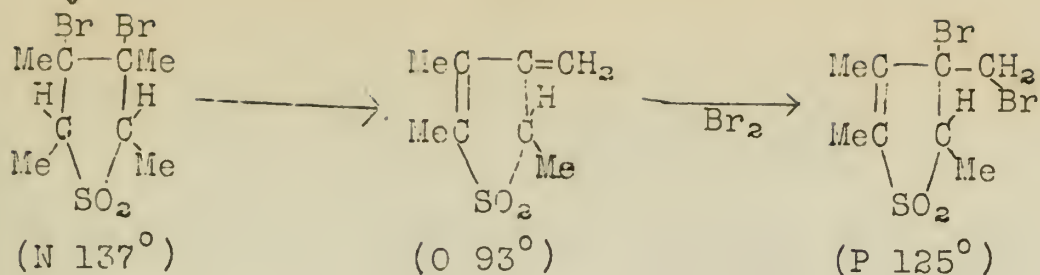
END OF PROBLEM SET 10

DATE	NAME
SCORE	GRADE
PROF.	TA

The addition of SO_2 to butadienes has been extended, and the structure of the resulting cyclic sulfones has been clarified by ozonizing them.

Structures for the following sulfones have been established:





Note that the sulfones of 2 tert.-butyl and of 2-phenyl-butadienes on ozonization form compounds which are isomeric with carboxylic acids, and may be termed isocarboxylic acids. These isocarboxylic acids in aqueous solution slowly isomerize to the ordinary acid according to law of monomolecular reactions.

Some of the butadienes isomerize in alkaline media when irradiated with ultra violet light. Ozonization studies indicate that this isomerization is not a cis-trans phenomenon, as Eigenberger supposed, but is due to a shift of the double bond.

Backer, Rec. Trav. Chim., 54, 170 (1935)
" " " " 53, 525 (1934)
" " " " 51, 395 (1933)

Eigenberger, J. Prakt. Chem., (2) 131, 289 (1931)
" " " " (3) 129, 312 (1931)
" " " " (2) 127, 309 (1930)

Stäudinger, Ber., 68B, 455 (1935)

Reported by Rene Oehler
April 15, 1936.

Hewett, J. Chem. Soc., 1936, 50.

Robinson and Walker, J. Chem. Soc., 1936, 192.

Cook and coworkers, Proc. Roy. Soc., 114B, 272 (1934).

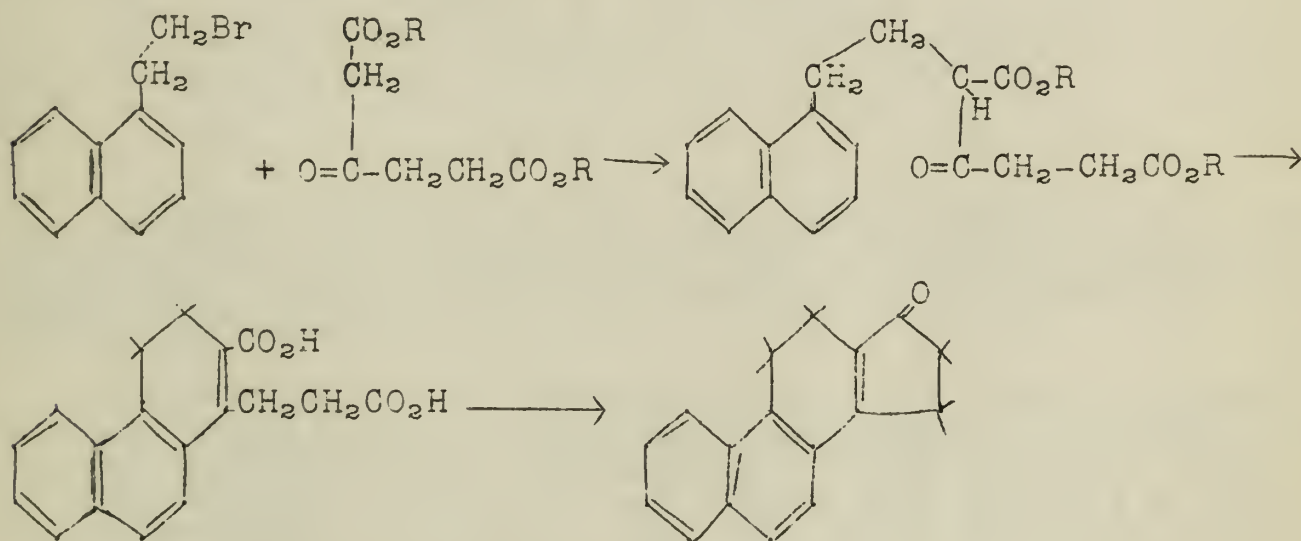
Bardhan, Nature, 134, 217 (1934).

The synthesis of fused ring systems related to the hormones has been actively pursued since the structure of oestrone has been established, and the discovery that other fused systems are active oestrogenically. Cook and coworkers have tested several types of fused ring systems and find that oestrogenic activity is not limited to types containing the ring system of oestrone but that other types are also active.

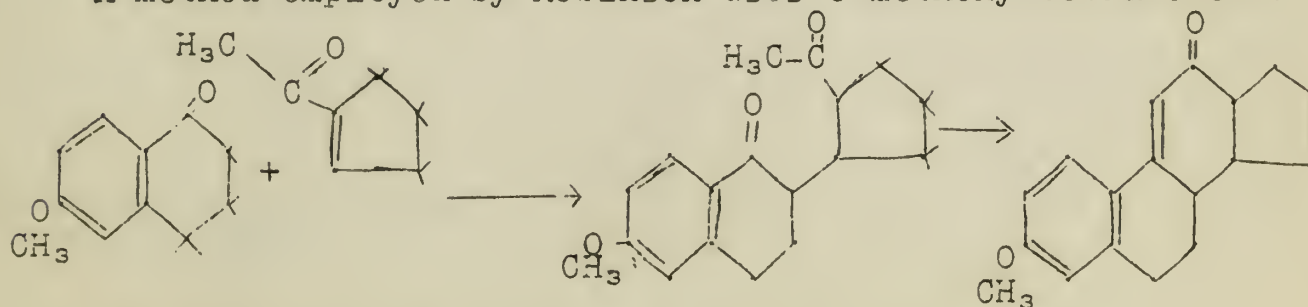
Examples of the last type are 1-keto-1,2,3,4-tetrahydro-phenanthrene and 9,10-dialkyl-9,10-dihydroxy-1,2,5,6-dibenz-anthracene.

Attempts to synthesize oestrone have so far been unsuccessful, but some of the compounds produced in these attempts possess oestrogenic activity and are quite closely related in structure to the natural hormone.

A method used by Bardhan for the preparation of this type of compound may be represented as follows.



A method employed by Robinson uses 6-methoxy-tetralone-1.



Other methods of preparation will be given.

SULFONATION OF NAPHTHALENE

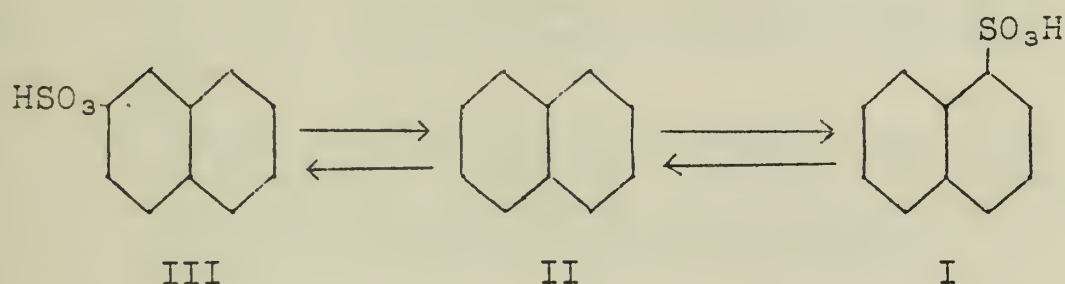
Lantz, Robert, Bull. Soc. Chim., (5) 2, 1913-32 (1935)
 ibid (5) 2, 2092-2108 (1935)

Research Laboratory of the Dye and Chemical Products
 Association of St. Denis.

Previous Work: Naphthalene bisulfite compounds.
 Naphthoquinone derivatives.
 Sulfur dyes.

The transposition of the α -naphthalene sulphonic acid I into the β -isomer may be explained on the basis of desulfonation and resulfonation in the β -position.

Lantz' work indicates the existence of an equilibrium:



At higher temperatures the rate of the reaction $I \longrightarrow II$ is accelerated while the reaction $III \longrightarrow II$ is relatively unaffected. This explains the formation of the β acid at higher temperatures.

A procedure for the determination of the relative amounts of the α and β acids in a mixture is presented. I is desulfonated and precipitated quantitatively as an insoluble polybromonaphthalene leaving III entirely in solution as a soluble polybromonaphthalenesulfonic acid. The insoluble product from I is then determined by CrO_3 oxidation.

Reported by L. L. Ryden
 April 22, 1936.

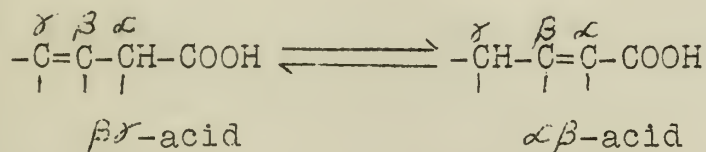
R. P. Linstead et al., Imperial College, London.

Work:

The authors have prepared a series of unsaturated acids and have studied the shift of the double bond and lactonisation under the influence of equilibrating agents such as, KOH, H₂SO₄ and heat alone.¹

I. Stability of unsaturated acids toward equilibrating agents. A study of tautomeric change.

- A. Comparative stability of isomeric $\alpha\beta$ - and $\beta\gamma$ -acids toward 25 per cent KOH at 100°C.² The general scheme for equilibria can be represented as follows:



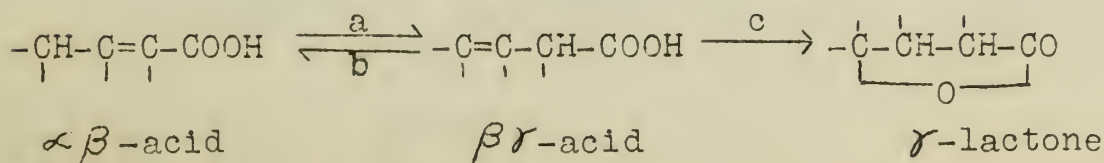
1. Butenoic acids without γ -substituents show no stability of the $\beta\gamma$ -form even when substituted on the β -carbon atom.
2. Butenoic acids with one γ -substituent show a small but definite stability of the $\beta\gamma$ -form, which is not appreciably affected by the nature of the substituent or the presence of an α -substituent.
3. γ -substituted butenoic acids having a second alkyl group on the γ -carbon atom show a great stability of the $\beta\gamma$ -form,³ and a similar but weaker effect is produced if the second substituent is on the β -carbon atom. The maximum effect in the β -position is given by an ethyl group.
4. These principles are still valid if the substituting groups form part of a polymethylene ring.^{3,4}

- B. The $\gamma\delta$ - and $\delta\epsilon$ -unsaturated acids⁵ show no tautomeric shift of the double bond when boiled with excess KOH, but are stable to this equilibrating agent.

II. Lactonisation and Tautomeric change. Equilibrating agent is H₂SO₄ (hot and cold--50 and 60 per cent) and sometimes heat alone.

- A. In the $\alpha\beta$ - and $\beta\gamma$ -series of unsaturated acids.

All acid-lactone systems of this kind can be interpreted by the one general scheme:



The following is a list of the names of the members of the American Medical Association who have been elected to the office of President for the year 1934-1935. The names are listed in alphabetical order of their last names.

A. J. McLaughlin, M.D., of Chicago, Ill., was elected President of the American Medical Association for the year 1934-1935.

The following is a list of the names of the members of the American Medical Association who have been elected to the office of President for the year 1934-1935. The names are listed in alphabetical order of their last names.

THE JOURNAL OF THE AMERICAN MEDICAL ASSOCIATION
PUBLISHED WEEKLY
CHICAGO, ILL., MAY 19, 1934

Page 7

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The variations between different systems can be attributed to differences in the ratio of the velocity of the tautomeric change (a and b) to that of ring closure (c). Four types of acids can be distinguished.⁶

1. Those in which both changes are slow but lactonisation is much faster than tautomeric change (acids with one α -alkyl and no β -alkyl substituent).⁶
2. Those in which lactonisation is fast and tautomeric change is slow (acids with two α -alkyl substituents).⁶
3. Those in which tautomeric change is faster than lactonisation (acids with one α - and one β -substituent).⁷
4. Those in which tautomeric change is fast and irreversible in the direction $\beta\alpha \longrightarrow \alpha\beta$, no lactonisation being possible (acids without α -substituents).⁸

B. In the α - δ series of unsaturated acids.⁹

In this series the exclusive reaction is lactonisation and no tautomeric change occurs. The direction of lactonisation (i.e. α -or δ -lactone formation) depends upon the substituents about the double bond.

Lactonisation, in the case of $\alpha\delta$ -acids having two δ -alkyl groups, is reversible by heat alone. Probably this is the "purest" example of ring-chain tautomerism:



C. In the $\delta\epsilon$ -series of unsaturated acids.⁵

Lactonisation was accompanied to an unusual extent by side reactions. Trustworthy experimental method for estimation of lactone content was not devised.

- D. Some unsaturated acids have been studied in which the double bond is farther removed from the carboxyl. They are reported to yield γ -lactones by action of conc. H_2SO_4 .¹⁰

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- Linstead, R. P. et al., J. Chem. Soc.
 (1) 1930, 1603; (2) 1928, 2343; (3) 1930, 2064; (4) 1935, 258; (5) 1934, 1995; (6) 1932, 115; (7) 1934, 599;
 (8) 1933, 577; (9) 1933, 580.
 (10) Zhukov, A. A. and Shestakov, P. I., J. Russ. Phys. Chem. Soc., 40, 830 (1908), cf. C.A., 3, 1148 (1909).

1. The first part of the report deals with the general situation of the country and the progress of the work during the year. It is divided into two main sections: the first section deals with the general situation and the second section deals with the progress of the work.

2. The second part of the report deals with the results of the work during the year. It is divided into two main sections: the first section deals with the results of the work in the field and the second section deals with the results of the work in the laboratory.

3. The third part of the report deals with the conclusions of the work during the year. It is divided into two main sections: the first section deals with the conclusions of the work in the field and the second section deals with the conclusions of the work in the laboratory.

4. The fourth part of the report deals with the recommendations of the work during the year. It is divided into two main sections: the first section deals with the recommendations of the work in the field and the second section deals with the recommendations of the work in the laboratory.

5. The fifth part of the report deals with the summary of the work during the year. It is divided into two main sections: the first section deals with the summary of the work in the field and the second section deals with the summary of the work in the laboratory.

6. The sixth part of the report deals with the appendix of the work during the year. It is divided into two main sections: the first section deals with the appendix of the work in the field and the second section deals with the appendix of the work in the laboratory.

7. The seventh part of the report deals with the bibliography of the work during the year. It is divided into two main sections: the first section deals with the bibliography of the work in the field and the second section deals with the bibliography of the work in the laboratory.

8. The eighth part of the report deals with the index of the work during the year. It is divided into two main sections: the first section deals with the index of the work in the field and the second section deals with the index of the work in the laboratory.

9. The ninth part of the report deals with the list of figures of the work during the year. It is divided into two main sections: the first section deals with the list of figures of the work in the field and the second section deals with the list of figures of the work in the laboratory.

10. The tenth part of the report deals with the list of tables of the work during the year. It is divided into two main sections: the first section deals with the list of tables of the work in the field and the second section deals with the list of tables of the work in the laboratory.

I

Methods of Analysis

The difficulty involved in quantitatively determining the deuterium content of organic-d compounds has recently aroused considerable attention. Compounds of molecular weight above 150 and of low deuterium content cannot be effectively analyzed by the ordinary methods of analysis. The following new procedures have been developed:

Combustion of the organic compound followed by a density determination of the resulting water using,

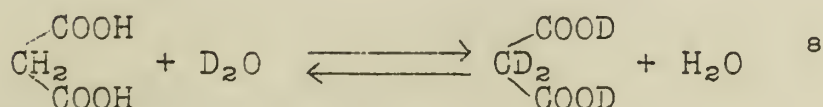
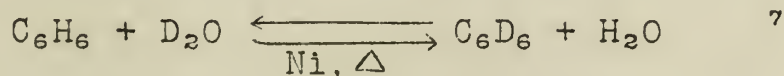
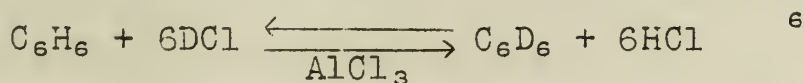
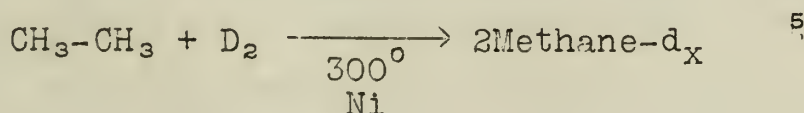
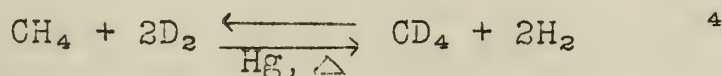
- a) The Zeiss interferometer method of density determination.¹
- b) The "submerged float" method.²
- c) The "swimmer" method.³

The merits of each of these will be discussed.

II

Organic-d Compounds

Deuterium has supplied the physical chemist with an excellent means of studying reaction kinetics. Cleavage of the carbon-hydrogen bond by exchange reactions with deuterium have been studied. The following exchanges have been shown to occur:



Although the majority of organic deuterium studies have been mainly physical in nature, Schoenheimer and Rittenberg⁹ have reported that deuterium is an ideal "indicator" in the study of intermediary metabolism. Since it is an isotope of hydrogen, the substitution of deuterium for hydrogen in food-stuffs has a distinct advantage over the introduction of such

ARTICLE 1

The first section of the constitution of the American Medical Association is devoted to the purpose of the association. It states that the purpose of the association is to advance the science and practice of medicine, to promote the health of the people, and to maintain the highest standards of medical education and practice. This purpose is to be achieved by the association through the cooperation of its members and the support of the public.

The second section of the constitution is devoted to the organization of the association. It states that the association shall be organized into a national association and into local associations in each state and territory. The national association shall be the supreme authority in the association, and the local associations shall be subordinate to it.

The third section of the constitution is devoted to the membership of the association. It states that the association shall be open to all persons who are qualified by education and experience to practice medicine. The association shall have the right to exclude from its membership any person who is not qualified or who is not in good standing with the medical profession.

The fourth section of the constitution is devoted to the officers and members of the association. It states that the association shall have a president, a vice-president, and a council. The president shall be the chief executive officer of the association, and the council shall be the governing body of the association.

ARTICLE 2

The first section of the second article of the constitution is devoted to the powers and duties of the association. It states that the association shall have the right to make and alter its constitution and bylaws, to elect and remove its officers and members, and to do all such other acts and things as may be necessary or proper to carry out its purpose.

The second section of the second article is devoted to the powers and duties of the council. It states that the council shall have the right to make and alter the bylaws of the association, to elect and remove its members, and to do all such other acts and things as may be necessary or proper to carry out its purpose.

The third section of the second article is devoted to the powers and duties of the president. It states that the president shall have the right to call and preside over the meetings of the association, to sign and execute all orders and resolutions of the association, and to do all such other acts and things as may be necessary or proper to carry out his duties.

The fourth section of the second article is devoted to the powers and duties of the vice-president. It states that the vice-president shall have the right to call and preside over the meetings of the association, to sign and execute all orders and resolutions of the association, and to do all such other acts and things as may be necessary or proper to carry out his duties.

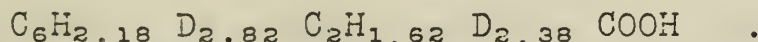
The fifth section of the second article is devoted to the powers and duties of the council. It states that the council shall have the right to make and alter the bylaws of the association, to elect and remove its members, and to do all such other acts and things as may be necessary or proper to carry out its purpose.

The sixth section of the second article is devoted to the powers and duties of the president. It states that the president shall have the right to call and preside over the meetings of the association, to sign and execute all orders and resolutions of the association, and to do all such other acts and things as may be necessary or proper to carry out his duties.

The seventh section of the second article is devoted to the powers and duties of the vice-president. It states that the vice-president shall have the right to call and preside over the meetings of the association, to sign and execute all orders and resolutions of the association, and to do all such other acts and things as may be necessary or proper to carry out his duties.

groups as halogen, phenyls, etc.; in addition, it enables the transportation of food-stuffs in the body to be easily traced. Stearic 6-7-9-10-d₄ acid and coprostanone 4-5-d₂ have been synthesized and their physiological fate observed.

In an effort to study the questionable asymmetry of the type R'R''CHD, Erlenmeyer and Gärtner¹⁰ prepared β -phenyl-propionic α -d, β -d acid by the deuterium iodide reduction of cinnamic acid. It was subsequently shown that this drastic reduction caused deuterium exchange to produce a product of the formula



On the assumption that part of the molecules would conform to the R'CHD-CHDR'' type, the strychnine salt was prepared and fractionally crystallized. No evidence of resolution was obtained.

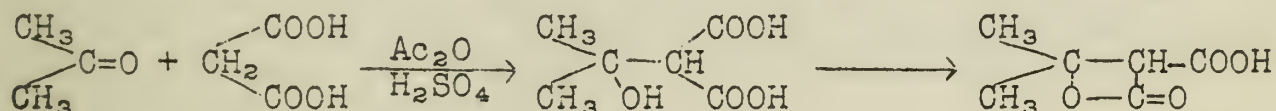
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2. Rittenberg and Schoenheimer, J. Biol. Chem., 111, 169 (1935)
3. Erlenmeyer and Gärtner, Helv. Chim. Acta, 19, 129 (1935)
4. Taylor and coworkers, J. Am. Chem. Soc., 57, 383, 592 (1935)
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Reported by Marlin T. Leffler
May 6, 1936.

Michael and Wiener, J. Am. Chem. Soc., 58, 680 (1936)
 Michael and Ross, J. Am. Chem. Soc., 55, 3684 (1933)
 Harvard University

A large literature exists on the use of malonic acid for the synthesis of α,β -unsaturated acids by condensation with aldehydes. Acetone does not show an analogous reaction, however, Meldrum¹ observed that addition of a small amount of sulfuric acid brought about an aldolization, involving the carbonyl group of the ketone, followed by an intramolecular esterification of the formed β -hydroxy acid to β ,3-dimethyl- β -propiolactonic acid, e.g.,



The Meldrum method was improved by Ott² in 1913 and since that time a number of β -lactonic acids have been prepared from ketones by use of the Meldrum-Ott method.

In 1933 Michael and Ross showed that aliphatic aldehydes may be substituted for ketones in the synthesis of β -lactonic acids. The most recent paper deals with the use of several aromatic aldehydes, e.g., benzoic, salicylic, acetylsalicylic and cinnamic aldehydes. Benzaldehyde gives the expected β -lactonic acid but the others lead to different products.

The β -lactonic acids formed by the condensation of benzaldehyde with malonic and methyl malonic acids are of special interest since they are the first proved β -lactonic acids with only one substituent in the β -position.

The thermal and chemical properties of the β -lactonic acids have been further studied and it has been shown that all compounds of this type are cleaved by heat and by alkali through the first-formed β -hydroxy malonates by rupture at the α,β -carbon linkage.

References:

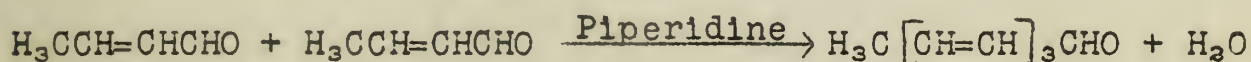
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2. Ott, Ann., 401, 151 (1913)

Reported by J. H. Brown
 May 6, 1936.

(Knoevenagel reaction)

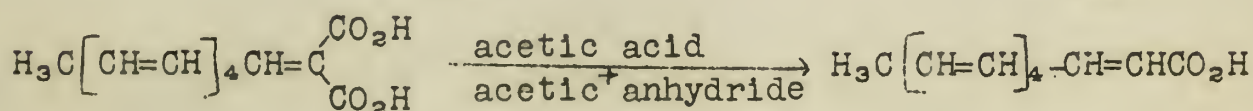
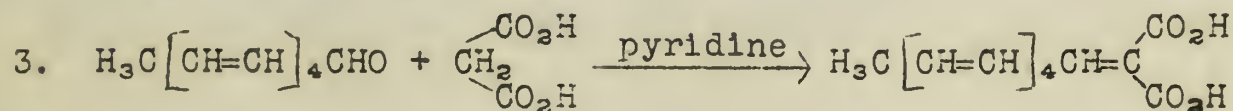
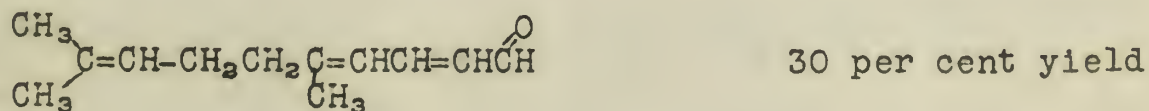
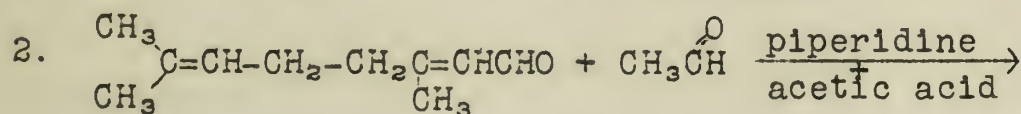
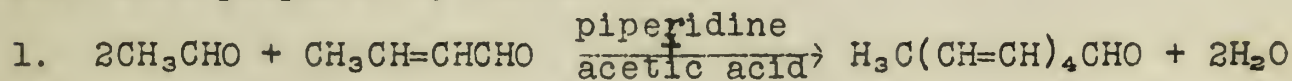
R. Kuhn, W. Bodstübner and C. Gundmann, Ber., 69, 98 (1936)
 R. Kuhn and M. Hoffer, Ber., 63, 2164 (1930)
 Blanchard, Klein and McDonald, J. Am. Chem. Soc., 53,
 2809 (1931)
 L. H. Smith and K. N. Welch, Jour. Chem. Soc., London,
 1136 (1934)

The action of secondary amines (piperidine) on acetaldehyde or on a mixture of acetaldehyde and crotonaldehyde, previously represented the best way of obtaining polyene aldehydes. In order to obtain octatrienal, $H_3C(CH=CH)_3CHO$, free from its neighboring vinyl homologs, R. Kuhn and M. Hoffer tried the condensation of crotonaldehyde with itself.



The condensation did not take place. If, however, the crotonaldehyde was exposed to sunlight then the addition of a small amount of piperidine caused the condensation to proceed as shown. The condensation goes equally well in the dark if crotonic acid, acetic acid or citric acid is added to the pure aldehyde. The active condensing agent, then, is the salt of the secondary amine instead of the amine itself as had previously been supposed.

From the foregoing facts the use of an amine salt is suggested for those condensations in which one of the reactants is not itself an acid. Such is the case of crotonaldehyde condensing with itself. The following unsaturated aldehydes and acid were prepared by the authors:

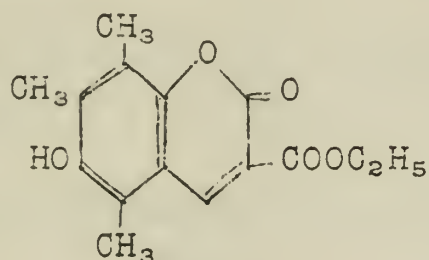


THE REACTIONS BETWEEN QUINONES AND SODIUM ENOLATES

Smith and MacMullen, J. Am. Chem. Soc., 58, 680 (1936)

Smith and Denyes, J. Am. Chem. Soc., 58, 304 (1936)

In 1926 Smith showed that 3-carbethoxy-5,7,8,-trimethyl-6-hydroxy coumarin resulted when duroquinone reacted with sodium malonic ester.



One of the methyl groups had taken part in this reaction.

Von Peckman, Ikuta, Graebe and Levy, and others have reported various products previously from quinones and sodium enolates.

Pseudocumonoquinone produces 5-hydroxy-2,4,6,7-tetramethyl coumarone and 5-hydroxy-4,6,7,-trimethyl isocoumaranone with sodium acetoacetic ester, and just the latter product with sodium malonic ester. No coumarin derivatives are formed.

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Smith and Dobrovolny, J. Am. Chem. Soc., 48, 1693 (1926)

Smith, J. Am. Chem. Soc., 56, 472 (1934)

Von Peckman, Ber., 21, 3005 (1888)

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Graebe and Levy, Ann., 283, 251 (1894)

Reported by R. C. Cary
May 13, 1936

HEATS OF HYDROGENATION OF OLEFINIC BONDS

G. B. Kistiakowsky et al., Harvard University

Previous work: Activated adsorption
 Kinetics of reactions
 1.) cis-trans isomerizations
 2.) thermal decompositions

For most organic reactions, heats of reaction must be calculated from notably unreliable heats of combustion. The more accurate, but somewhat more difficult, direct calorimetric determination of heats of reaction has only occasionally been used.

Kistiakowsky and his coworkers plan to systematically develop this method, and at present are studying the heats of hydrogenation of olefinic compounds. To date, four papers have been published, and the data recorded is summarized in the following tables.

Heats of Hydrogenation of Mono-olefins

Compound	ΔH_{3550}	Compound	ΔH_{3550}
ethylene	-32,824	isobutene	-28,389
propylene	-30,115	<u>unsym</u> -methylethyl-	
butene-1	-30,341	ethylene	-28,491
<u>n</u> -heptene-1	-30,137	<u>unsym</u> -methylisopropyl-	
<u>cis</u> -butene-2	-28,570	ethylene	-27,997
<u>trans</u> -butene-2	-27,621	pentenes-2	-27,954
		trimethylethylene	-26,920
		tetramethylethylene	-26,663

Heats of Hydrogenation of Dienes and Cyclic Olefins

Compound	ΔH_{3550}	Compound	ΔH_{3550}
allene + 2H ₂	-71,280	cyclohexene + H ₂	-28,592
1,3-butadiene + 2H ₂	-57,067	1,3-cyclohexadiene + 2H ₂	-55,367
1,4-pentadiene + 2H ₂	-60,790	benzene + 3H ₂	-49,802
1,5-hexadiene + 2H ₂	-60,525	cyclopentadiene + 2H ₂	-50,865

ΔH , the heat of reaction, may be defined as the heat absorbed in calories when one mol of reaction occurs at constant pressure. In the above tables ΔH is recorded at 355° K (83° C) at which temperature the reactions were carried out.

By combining certain of the above values the heats of reaction for several interesting reactions may be calculated.

allene + H ₂ \longrightarrow propylene	$\Delta H_{3550} = -41,165$
1,3-butadiene + H ₂ \longrightarrow <u>n</u> -butene-1	$= -26,720$
1,4-pentadiene + H ₂ \longrightarrow <u>n</u> -pentene-1	$= -30,660$
1,5-hexadiene + H ₂ \longrightarrow <u>n</u> -hexene-1	$= -30,400$
1,3-cyclohexadiene + H ₂ \longrightarrow cyclohexene	$= -26,700$
benzene + H ₂ \longrightarrow 1,3-cyclohexadiene	$= + 5,570$

If an increase in ΔH may be interpreted as indicative of increased stability of the double bond, the following conclusions may be drawn.

- 1.) For simple olefins, substitution on the carbons carrying the double bond increases the stability of the bond.
- 2.) For dienes:
 - (a) The allene type is the least stable.
 - (b) The double bonds in a conjugated system are the most stable.
 - (c) As the distance between the double bonds is further increased, the stability of the bonds approaches that of the simple olefin bond.
- 3.) In benzene, which may be considered a "continuously conjugated" system, an unusually stable type of unsaturation is present. It has been suggested that this condition be used as the criterion for aromaticity.

References

- G. B. Kistiakowsky et al., J. Am. Chem. Soc., 57, 65 (1935)
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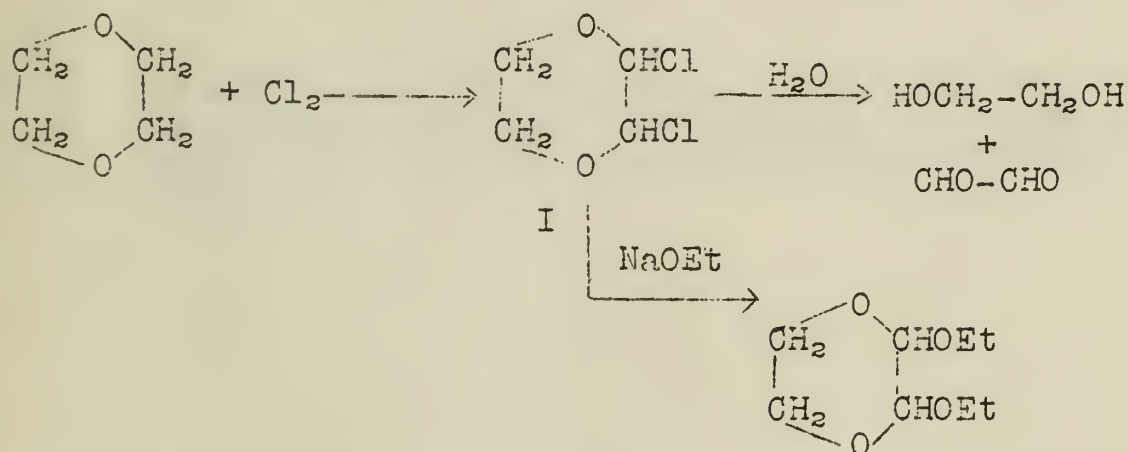
Reported by M. F. Roy
May 20, 1936.

DIOXANES

- Boesekin and coworkers, Rec. trav. chim., 53, 1067 (1933)
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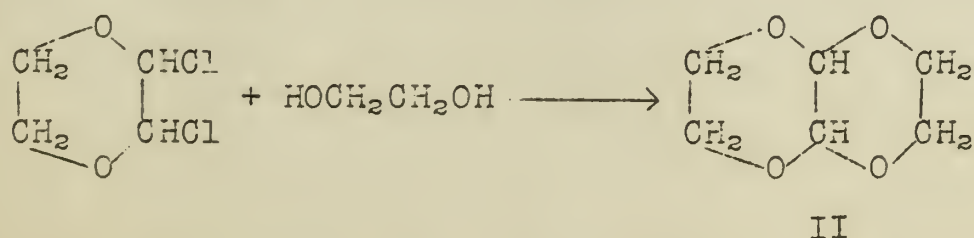
Dioxane was first prepared by several independent investigations in 1863. Although these initial works were followed by many others, the only results obtained were summarized in a characterization of the physical properties of the compound and in the observation that it was surprisingly resistant to most chemical reagents. It was observed that the compound formed many molecular compounds with several series of reagents.

Boesekin, in very recent years, observed that dioxane reacted with chlorine to produce a dichlorosubstituted dioxane which was shown by hydrolysis to be the 2,3-dichlorodioxane, (I). This hydrolytic reaction was an indication of the activity of the chloro substituents toward other reagents.



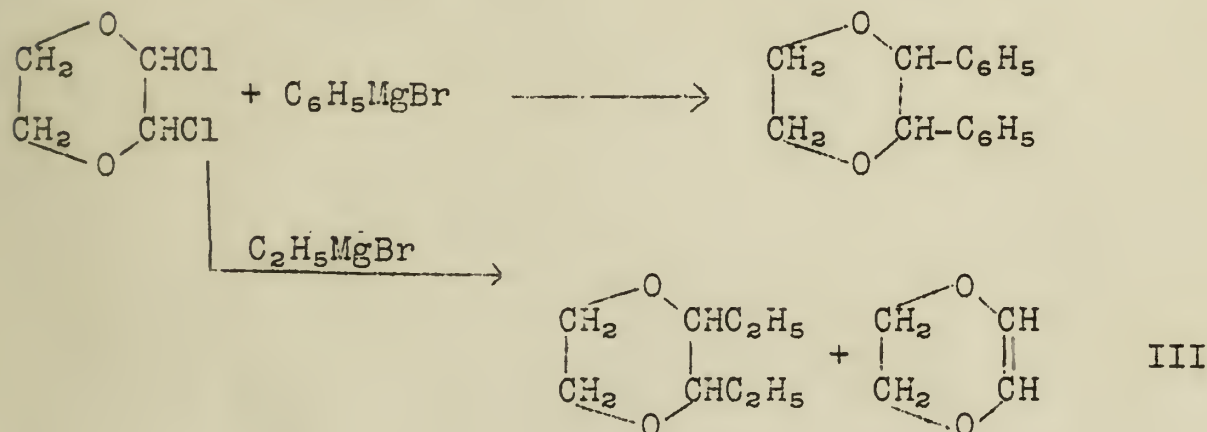
Subsequent work on the chemistry of dioxane has always involved this primary chlorination of dioxane, and can be divided into the following types:

1. Formation of fused ring systems containing the dioxane nucleus. As an example naphtho-dioxane, (II) was formed by the action of ethylene glycol on 2,3-dichlorodioxane.



From this reaction two isomers were obtained. They were analogous to the cis-trans isomers of decalin.

2. Higher chlorinated dioxanes.--2,3-Dichlorodioxane and chlorine produced several isomeric tetrachlorodioxanes, the structures of which were determined by hydrolysis. The symmetrical tetrachlorodioxanes were quantitatively hydrolyzed to glyoxal.
3. Other disubstituted dioxanes and their reactions.--The activity of the chloro substituents of the 2,3-dichlorodioxane was further evidenced by the reaction with Grignard reagents.



The p-dioxene, (III) was shown to add chlorine, bromine and hydrogen bromide. The addition of hydrogen bromide served as a basis for the mechanism of chlorination of dioxane.

Reported by L. L. Alexander
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